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ION EXCHANGE BETWEEN SOLIDS AND SOLUTIONS.

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INTRODUCTION.

Ion exchange may be defined as a reversible interchange of ions between a liquid phase and a solid body which does not involve any radical change in the solid structure. It was first observed in soil by Way in 1850 (72). He passed a solution of potassium chloride through a bed of soil, and found that all the potassium was removed from the solution and replaced by an equivalent amount of calcium and sodium from the soil. Since that time, a wide variety of solid bodies have been found to take part in ion exchange, and some of them are of great practical value. Both cations and anions may take part in ion exchange, but the exchange of cations is much more common.

In the first part of this paper, the substances that show ion exchange will be reviewed, and their structure and properties noted. The second part of the paper will deal with the physical chemistry of the actual exchange process, and, in particular, with the equilibrium between ions in the solution and ions in the exchanger, while the last part will discuss some of the technical applications of ion exchange.

PART I.

MATERIALS SHOWING ION EXCHANGE.

Ion Exchange in Minerals.

Among the minerals in which ion exchange is most marked are aluminosilicates such as the zeolites, montmorillonite and some other clay minerals, ultramarine, glauconite and the chabazites. A smaller degree of ion exchange is found in the felspars and kaolinite. All of these minerals contain alkali or alkaline earth metal ions, and it is these ions which will exchange with ions in solutions.

In order that ions may pass in and out of the body of the mineral and so effect ion exchange, a certain openness of structure of the solid is necessary. The degree of openness of silicate crystals can be seen in part from their volumes per structural oxygen atom; examples of such volumes are given in Table I. From the table it can be seen at once that a large crystal volume per oxygen atom is associated with a large ion exchange. Garnet, with the smallest volume per oxygen atom, has no ion exchange power, while glauconite, with the largest volume, has the largest ion exchange power. However, the correlation is not perfect. Orthoclase, nosean and ultramarine have the same volumes per oxygen atom and yet differ greatly in ion exchange; orthoclase has to be heated in a sealed tube with the exchanging solution before much exchange takes place, while ultramarine exchanges a portion of its ions rapidly at room temperature. These differences, especially the difference between nosean and ultramarine which have the same chemical composition as well as the same crystal volumes, show that other structural factors besides the average density of the crystal lattice influence the ease of ion exchange. These will be discussed in more detail.

TABLE I.

Mineral.	Formula.	Volume per Oxygen Atom.	Cation Exchange.
Garnet	$Mg_3Al_2Si_3O_{12}$	15.4 Å^3	None
Muscovite (a mica)	$K_2Mg_6Al_2Si_6O_{22} \cdot H_2O$	19.2	Slight
Orthoclase (a felspar)	$KAlSi_3O_8$	23.0	Slight
Nosean	$Na_5Al_3Si_3O_{12}(SO_4)$	23.1	Fair
Ultramarine	$Na_5Al_3Si_3O_{12}(SO_4)$	23.1	Very good
Apophyllite	$KCa_4Si_8O_{20}F \cdot 8H_2O$	26.8 *	Good
Natrolite (a zeolite)	$Na_2Al_2Si_3O_{10} \cdot 2H_2O$	28.0	Very good
Glauconite	$K(Fe, Al)Si_2O_6$	About 28	Excellent

* Fluorine atom is counted as an oxygen atom. St. Naray-Szabo, ref. 64; Mellor's Treatise, Vol. 6, p. 920, for glauconite.

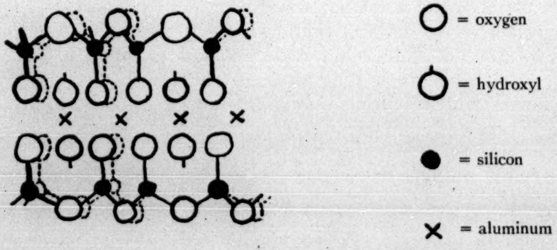
Zeolites, Ultramarines, Scapolites.—Aluminosilicate crystals are built up of tetrahedra whose four corners are taken up by oxygen atoms and whose centers are atoms of silicon or aluminum. The tetrahedra are linked together through their corners, that is, by the oxygen atoms. In the zeolites, ultramarines and scapolites, they are arranged in small frameworks which in their turn are joined into long straight strings, which run through the whole crystal, and are held together by valency forces to make a criss-cross network. The networks are of such a shape that wide straight channels 5–6 Å. in diameter are left running through the crystal. It is these channels which permit easy diffusion of ions through the entire crystal, and which, therefore, are essential to ion exchange.

In the *zeolites*, the channels do not intersect, but the alkali metal ions lie between them, so that they can escape into one channel or the other when ion exchange takes place. The channels themselves are ordinarily filled with water molecules.

This structure of the zeolites explains their characteristic easy loss of water, their high electrical conductivity (73), and the high porosity and absorbing qualities of dehydrated zeolites. In the *ultramarines*, the channels intersect and in doing so form large cavities, in which the cations and the anions (which also are exchangeable) reside (56, 65). The *scapolites* have a similar cavitied structure; they are isomorphous mixtures of two end-members, marialite, $Na_4Al_3Si_9O_{24}Cl$, and meionite, $Ca_4Al_6Si_6O_{24}(SO_4, CO_3)$, and can exchange both anions and cations. *Sodalite*, $Na_4Al_3Si_3O_{12}Cl$, has a structure of the same kind, and exchanges its chloride ions for sulfate on fusion with sodium sulfate (57).

Glauconite.—The mineral glauconite is the main constituent of greensand, where it occurs as rounded granules which appear to be amorphous, but which X-ray diffraction shows to be aggregates of micro-crystals. It has a permeability to ions which is even greater than that of the zeolites, probably because the exchanging ions can diffuse between the crystal units even more readily than they can diffuse within them.

Montmorillonite.—An interesting mineral intermediate between the zeolites and felspars in ion exchange and demonstrating a different kind of channeled crystal structure from the zeolites is montmorillonite, the main constituent of bentonite clay. It has the approximate composition $AlSi_2O_5(OH) + nH_2O$; part of the aluminum is replaceable, that is, it occurs as mobile ions rather than as rigid lattice units, and in nature it is partially replaced by iron, magnesium, and other ions. The crystal structure of montmorillonite is as follows (33, 34):



The crystal unit consists of two layers of silicon and oxygen atoms with a space in between, where the aluminum ions (except for some which replace silicon atoms here and there) and other replaceable ions, such as magnesium, are located. This planar space is to some extent analogous to the tubular channels in a zeolite, and should permit free access of ions to the whole crystal. Ionic replacement in montmorillonite, however, is not as easy as in a zeolite. The amount of exchange possible is smaller, about 1 m. eq./gram as compared with 3 m. eq./gram in a zeolite. There is evidence that the exchanging ions do not all enter the central channel, but stay outside the crystal unit, between the parallel Si-O planes of neighboring units; this evidence comes from the effect of ion exchange on the characteristic swelling which montmorillonite undergoes when placed in water (53). It would seem that the planar cavities which are only open to the outside on the small peripheral faces of the sheet-like crystals do not offer as much chance for diffusion of ions into them as do the tunnels of a zeolite crystal. Moreover, the channels of montmorillonite are only wide enough to admit small ions such as sodium or calcium, and not the larger cations (see page 308).

The permeability of montmorillonite relative to that of the zeolites is seen from the effect of powdering on ion exchange. The exchange capacity of a zeolite increases with decreasing particle size only up to a certain point (reached with greensand at 80 mesh) after which increasing subdivision has no effect (7), whereas the capacity of montmorillonite for ion exchange continues to increase down to very small particle size, though the capacity does not increase as fast as surface area (33).

Apophyllite.—Apophyllite is another cation exchanging mineral showing a layered structure. The structure allows diffusion of ions between Si-O layers, as does that of montmorillonite, and it also has gaps in the Si-O layers themselves which permit the passage of ions (46, 66). Apophyllite is interesting in that it contains no aluminum, showing that it is not necessary for a mineral to be an aluminosilicate to have exchangeable cations, but that some sort of channeled crystal structure is the important factor.

Apatite.—Exchange of anions alone is shown by apatite, a calcium phosphate of formula $3Ca_3PO_4 \cdot Ca(F, Cl)_2$, and better by phosphate rock, which consists of micro-crystals of apatite. The halogen ions can be exchanged for other halogen ions, and for hydroxide and, to some extent, other ions in aqueous solution.

Synthetic Inorganic Ion Exchangers.

Aluminosilicates Made by Fusion.—For technical water treatment, synthetic aluminosilicates have displaced natural base exchanging minerals in many fields of use. The first synthetic materials to be used commercially were made by fusing mixtures of quartz, clay, and soda ash. China clay has the composition $Al_2Si_2O_7$; when fused with sodium carbonate and quartz this gives a glassy, amorphous mass containing a greater proportion of silica to alumina than was present in the clay. The composition desired was generally $Na_2Al_2Si_3O_{10}$. All the sodium, and any calcium present from impurities in the clay, could be replaced by other cations by treatment with aqueous solutions of these cations (29, 40).

The rate of diffusion of ions into such aluminosilicates prepared by fusion was faster than that into natural crystalline zeolites (29), but it was, nevertheless, so slow that inconveniently long periods were required for softening and regeneration when the materials were used as water softeners. The mineral glauconite was much more rapidly acting, and so displaced synthetic aluminosilicates prepared by fusion as a water softening material (12).

Aluminosilicates Made by Precipitation.—A second class of synthetic aluminosilicates, having a much higher permeability to ions, is made by mixing sodium silicate with sodium aluminate or aluminum sulfate, or both, in aqueous solution. A gelatinous precipitate separates, or a gel is formed, according to the conditions. Gelatinous precipitates have been used as bases for making water softening materials (14), but the gel type is by far the more important. The gel is pressed and dried until opaque horny lumps are left. On wetting these again with water, they disintegrate into small granules of about the right size for use in water softening. These have a large ion exchange capacity, react very quickly with aqueous solutions and, although rather sensitive to attack by carbonic acid, are not so susceptible as the fused aluminosilicates (12). On account of their high capacity and rapidity of reaction, they have displaced glauconite except in fields where the greater density of glauconite and its greater resistance to chemical attack render it more suitable.

The gel type aluminosilicates have the formula $Na_2O \cdot Al_2O_3 \cdot nSiO_2 \cdot xH_2O$ where n is generally 5 or 6. Materials with $n = 12$ are also used where resistance to chemical attack is needed. The ion exchange capacity seems to increase with increasing $SiO_2 : Al_2O_3$ ratio up to about 6 : 1, after which it falls slowly (48, 77). It is suggested that the optimum Si : Al ratio corresponds to an optimum interatomic spacing at which the permeability to ions, and the spatial and electrostatic requirements for holding replaceable ions in the solid granules, together produce the maximum exchange capacity.

The granules of synthetic aluminosilicate retain their gel structure and are amorphous. They are easily permeable to water and small ions, but not to large ions and molecules such as quaternary ammonium cations or sugar or methylene blue molecules (77, 78). Cane sugar molecules have diameters of about 5 Å; trimethylammonium ions, which can enter the gel, but with difficulty, have diameters of about 3.9 Å. The pores of the gel must, therefore, be 4 − 5 Å. in diameter. This is of the order of the width of unit cells of SiO_2 or Al_2O_3, and is abnormally small; for the pores of silica gel or cocoanut charcoal are about 50 to 60 Å in diameter (23).

The gel type aluminosilicates have even smaller pores than the crystalline zeolites, and yet they exchange their ions much faster with solutions. This could be due to a larger number or more favorable arrangement of pores in the gels, and also to a weaker chemical binding of the ions in the solid. The latter explanation is suggested by comparing the electrical conductivity of an artificial aluminosilicate with that of a zeolite mineral; in the latter, the water of hydration carries the current, while in the former, the exchangeable cations migrate (20, 30, 72).

Gel type aluminosilicates can be heated to 200° C. without loss of ion exchange, but, when heated to redness, they sinter and lose practically all of their ion exchange power. Contact with solutions containing ferric ions or chromium ions lowers their ion exchange, because of exchange of some of the aluminum for iron or chromium (8), an exchange which is virtually irreversible.

Miscellaneous Cation Exchangers.—Materials can be prepared in which all the aluminum of the aluminosilicate is replaced by iron, manganese, boron, and other elements. They take part in ion exchange, but not to so great an extent as the aluminosilicates (8, 62). It is also possible to prepare silicates which contain no trivalent metal at all and yet show ion exchange, for example, by mixing sodium sulfate, zinc sulfate, and sodium silicate solutions, or simply by mixing sodium silicate and sulfuric acid solutions in the right proportions (13).

Calcium Phosphate.—Basic tricalcium phosphates similar in composition to hydroxyapatite are prepared by precipitation as hard gels, very permeable to water, and capable of exchanging their hydroxyl ions for fluoride ions. Other anions are too big to enter the solid structure to any appreciable extent. The power of taking up fluoride ions from water is of great value, however, for one or two parts of fluoride ions in a million of water causes mottling of the dental enamel in children, and water supplies in several localities contain much more than this amount. The fluoride can be removed by passing the water over a bed of basic tricalcium phosphate, and, when the bed can take up no more fluoride, it can be regenerated by passing sodium hydroxide solution (2).

Miscellaneous Anion Exchangers.—By mixing barium chloride and silicic acid solutions, a precipitate $Ba_2SiO_3Cl_2$ can be made which will exchange its chloride ions for bromide and other anions in aqueous solutions. Basic borates, stannates, and other salts of divalent metals can be prepared which contain replaceable anions, while an addition compound of barium tellurate with nitric acid, which has exchangeable nitrate ions, is known (71).

Ion Exchange in Organic Compounds.

The chief natural products which show ion exchange are the humic acids and the proteins. The latter, being amphoteric, can exchange both anions and cations, whereas the former can exchange only cations. In addition to these, a large number of carbon compounds having ion exchange have been made artificially, either from natural materials as a starting point or by synthesis from simple molecules. The carbonaceous ion exchangers are of special interest, because they are insoluble in acids, and so permit hydrogen ions to be exchanged just as any other cations. In siliceous exchangers this is impossible, unless the acid concentration is kept extremely low (16, 61).

Humic Acids.—Much of the ion exchange power of soil is is due to the humic acids which are present. The exchange is especially high when the soil is almost entirely of vegetable origin. Peat, for example, contains a considerable quantity of exchangeable hydrogen ions. Lignite and brown coal contain enough humic acids to give them appreciable exchange power; their humic acid content can, of course, be increased by mild oxidation.

Proteins.—All proteins on the negative side of their isoelectric point contain replaceable hydrogen ions, and insoluble metallic derivatives can be prepared which show cation exchange. *Casein* is a substance which has been studied in this way (27); it contains about 1 m. eq. of replaceable hydrogen ion per gram. *Wool* is ordinarily on the positive side of its isoelectric point and will take up acids from solution, which is the reason that it is easily dyed by acid colors. The anions taken up can be exchanged for others in the usual way.

Products from Coal and Wood.—Lignite, after mild oxidation with moderately concentrated nitric acid, shows considerably increased cation exchange, on account of increase in its humic acid content (10, 38). Coal, lignite, and wood give cation exchanging products on treatment with dehydrating agents such as phosphoric acid or zinc chloride (9, 59). Wood products, such as paper, often have a little cation exchange, due to the lignin sulfonic acids or other lignin derivatives present (45).

Of major commercial value are the products of high cation exchange power which are obtained from bituminous coal by the action of concentrated sulfuric acid or sulfur trioxide (51). This reaction is very complex, involving oxidation, sulfonation, and some dehydration. The product contains some six per cent. of sulfur, presumably as sulfonic acid groups. One experimenter found that the ion exchange capacity of sulfuric acid-treated coals was directly proportional to the sulfur content (27), which would indicate that all the exchange was due to sulfonic acid groups, but other evidence contradicts this view. The structure of sulfuric acid-treated coal is very little understood. It may, however, contain graphitic acid, a substance which is known to show cation exchange (36, 67).

Physically, the granules of sulfonated coal are about the same size, shape, and appearance when dry as the coal granules from which they were derived. They are hygroscopic, however, and absorb up to twenty-five per cent. of their weight of water from a moist atmosphere; when placed in water, they swell instantly to about thirty per cent. above their original size, and are very easily permeable to water and ions. The swelling is reversible. The material behaves, therefore, like an elastic gel. The base exchange power is about 1.5 to 2.5 m. eq. per gram dry weight.

The great commercial importance of these materials is due primarily to their resistance to acids. The implications of this fact will be discussed further in Part III. A second reason for their importance is that they do not impart any silica to the water which percolates through them, and, hence, can be used to soften water for high pressure boilers. A limitation which these materials have, however, is that in alkaline solutions they show a tendency to peptize.

Synthetic Resins.—The condensation products of formaldehyde with phenols, especially polyhydric phenols, contain large amounts of replaceable hydrogen ions (1). A catechol-formaldehyde resin, for instance, has 11 to 14 m. eq. of exchangeable cations per gram (3). In spite of this large potential capacity, however, these resins have little practical value, because their reaction with aqueous solutions is extremely slow (3). The slowness of exchange is not due to the narrowness of the channels in the resin mass; for these are some 10 Å. wide (3), or twice the width of the channels of an aluminosilicate gel. It must rather be due to the scarcity or unfavorable arrangement of such channels.

Not all ion exchanging resins are as slow to react as these. A class of resins having high permeability and speed of reaction, as well as good capacity, has been developed recently (50*a*).

Tannins (1), lignin sulfonic acid (24), and casein (27) can be condensed with formaldehyde to give insoluble resins with cation exchanging power. The exchange of tannin and lignin resins can be improved by sulfuric acid treatment, before or after condensing with formaldehyde (15). Polystyrene resins can be sulfonated to give cation exchangers, and polyalkyl acrylate resins can be partially saponified to give a carboxylic resin cation exchanger (9), but these are of little importance.

Basic resins which absorb acids from solution can be made by condensing aromatic amines or diamines with formaldehyde (1). The black exidation products of aniline; e.g., emeraldine, have similar properties. The absorption of acids is, in itself, not a process of ion exchange, for it can be shown that, when emeraldine (for instance) reacts with hydrochloric acid, it does so by direct addition:

$$R_3N + HCl = R_3NH^+ \cdot Cl^-$$

and not by exchange of hydroxyl ions. However, the chloride ion, when once absorbed, can be exchanged for other anions. such as sulfate, in the usual way.

Ion Exchange on Colloidal Particles.

Colloidal particles suspended in an ionizing liquid ordinarily carry a double layer of electric charge at their surface. The inner layer is due to ions attached firmly to the particle by chemical forces. The outer layer is made up mainly of ions of opposite charge held by electrostatic forces. It is diffuse in nature. Some of the ions are close up to the particle, and move with it in an electric field, whereas others are further away and contribute to some extent to the ionic activity of the solution. All the ions in the outer layer can be displaced by other ions added to the solution.

For example, the particles of a platinum sol prepared by electrical dispersion carry a negative charge, due to adsorbed hydroxyl ions or to the formation of an ionized surface oxide. Next to the negatively charged surface is a layer of hydrogen ions. When a solution of silver nitrate was added to such a sol, some of the hydrogen ions were liberated into the solution, and silver ions took their place. The silver ions could be displaced by barium ions, and so on, the quantity of ions exchanging being about 0.2 m. eq. per gram of platinum (58). The inner negatively charged layer did not exchange at all with the anions of the solution.

Similar experiments have been made with positively charged sols of hydrated ferric oxide and aluminum oxide. The positive charge is due to a firmly bound layer of hydrogen ions, which cannot be displaced except by a fairly high concentration of hydroxyl ions. Sols were prepared having chloride ions in the outer layer, and to them was added small amounts of sodium sulfate solution. The sulfate ions were taken up completely by the colloidal particles, and chloride ions appeared in the solution. The displacement of chloride ions (determined electrometrically) was less than the adsorption of sulfate ions (74). This is understandable, because the sulfate ion has a greater charge and polarizability than the chloride ion, and a greater proportion of sulfate ions than of chloride ions will be adsorbed close to the surface of the particle, where they cannot contribute to the ion activity of the solution.

The quantity of replaceable ions carried by such colloidal particles is 1 m. eq. or more per gram of metallic oxide, which is large enough to be of practical use. Ferric oxide gel carrying adsorbed hydroxyl ions has been used to remove acids from water (9, 26). Gels of aluminum and ferric oxides, also activated alumina, have been used to remove fluoride ions from water by anion exchange. They are first treated with dilute acid to make them positive colloids, the fluoride-bearing water is then passed, and the adsorbed anions in the gel are displaced by fluoride ions. Then, when the gel is loaded with fluoride ions, it is regenerated by passing sodium hydroxide to replace the fluoride, then dilute acid to neutralize excess of alkali and to restore the positive charge of the gel (17, 26).

The ion exchanging power of finely divided clays, such as china clay, can be attributed to the layer of adsorbed ions which they carry by reason of the negatively charged oxygen atoms at the crystal boundaries (42).

PART II.

DISTRIBUTION OF IONS BETWEEN CATION EXCHANGERS AND SOLUTIONS.

Introductory.

The equilibrium distribution of two or more ionic species between a solid cation exchanger and a solution has been investigated for many different materials, and there is a mass of data, of varying quality, recorded in the literature. Most of the work has been done on synthetic aluminosilicates of the gel and fusion types. Clays and bentonites have been investigated fairly thoroughly; greensand and natural zeolites less thoroughly. The data on organic exchangers are scanty, being limited to a paper on casein and some preliminary studies on synthetic resins and sulfonated coals. No data have been published on anion exchange equilibria.

The experimental procedure has generally been to start with an exchanger containing only one replaceable cation, and to shake this with a solution containing another cation for periods varying from half an hour to several days, depending on the speed of reaction of the material chosen. When no further exchange seemed to be taking place, the solution and, in some cases, the exchanger also was analyzed and the amount of exchange determined. This was repeated for different ratios of the ion in the exchanger to the replacing ion in the solution, and for different concentrations of solution.

In some cases, the distribution was approached from both sides of the final equilibrium; that is, starting first with ion *A* in the exchanger and ion *B* in the solution, then with ion *B* in the exchanger and ion *A* in the solution. As a rule, different distributions would be reached in the two cases, the tendency being to retain in the exchanger the ion with which it was originally saturated (61). Complete equilibrium apparently was not reached, save in one or two isolated cases.

This fact at first sight reduces the value of almost all the published measurements of ion exchange distributions. It is possible, however, that the characteristics of an ion exchanger are conditioned by the nature of the ion with which it was last saturated; that is, that an exchanger which has been saturated with calcium ions *ipso facto* gives an equilibrium curve distinct from that of the same exchanger saturated with sodium ions, and does not change until it is saturated or nearly saturated with another ion. In this case, results obtained, say, with a calcium exchanger and a series of other cations would be comparable. This idea was suggested by Patton and Ferguson (55) and is borne out by experiments of the writer.* It is also very likely that in many experiments the time allowed was not sufficient to reach equilibrium. Even though most of the exchange may be very rapid, the last ten or twenty per cent. is often extremely slow, especially when the displacement of one cation by another is nearly complete (21, 55).

In spite of the probable failure to reach equilibrium in cation exchange studies, experimental data are sufficiently consistent that a number of general relations can be inferred. These will be discussed in the paragraphs which follow. It is interesting to note that the relations hold for all types of cation exchanger, inorganic or organic.

Equivalence of Exchange and Anion Adsorption.

The fact that one ion replaces another in exactly equivalent proportions was observed by Way in his pioneer researches with soils, and has been confirmed by other workers for clays, zeolites, and artificial aluminosilicate exchangers (40, 61, 63). In certain cases, however, anion adsorption or desorption is found to accompany cation exchange, so that the exchange is not exactly equivalent. If, for instance, an exchanger containing barium ions is shaken with a small amount of sodium hydroxide solution, barium is exchanged for sodium, but, at the same time, hydroxyl ions are adsorbed from the solution, so that the sodium entering the exchanger has to be more than equivalent to the barium leaving it, to maintain electrical neutrality. Chloride and other anions are adsorbed in the same way, the adsorption being greater, the greater the valency of the cation in the exchanger. For example, in certain experiments a gram of sodium aluminosilicate adsorbed 0.03 m. eq. Cl^-, a gram of magnesium aluminosilicate adsorbed 0.26 m. eq., and a gram of aluminum aluminosilicate adsorbed 0.65 m. eq. (40). Adsorption increases, too, with the valency of the anion.

Casein carrying exchangeable divalent cations shows strong anion adsorption in aqueous alcoholic solutions. It is related to the concentration in solution by the Freundlich isotherm (27).

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* *Transactions Illinois Academy of Sciences*, forthcoming.

The non-equivalence of ionic exchanges in colloidal suspensions such as china clay is not necessarily due to anion adsorption. It has been discussed above (page 316).

Existence of a Single Solid Phase.

As more and more sodium ions are added to a solution which is in contact with an exchanger containing replaceable potassium ions, the ratio sodium : potassium in the solid increases continuously, showing no sharp jump at any point; the plot of this ratio against the sodium : potassium ratio in the solution is a smooth curve. This is true for all ion exchanges, and means that at no stage in the replacement of one ion by another does a second solid phase appear.

Exceptions to this behavior were reported for two exchanges by Rothmund and Kornfeld (63), but they have not been confirmed, and may safely be disregarded.

The Distribution Equation.

The simple law of mass action, which for ions of equal valency is

$$\left(\frac{c_1}{c_2}\right)_{\text{solid}} = K\left(\frac{c_1}{c_2}\right)_{\text{solution}}, \tag{1}$$

where c_1, c_2 are concentrations of ions 1 and 2, is obeyed in only a very few cases of cation exchange (4, 11, 50). More generally, the observed results can be expressed by the equation

$$\left(\frac{c_1}{c_2}\right)_{\text{solid}} = K\cdot\left(\frac{c_1}{c_2}\right)^{p}_{\text{solution}}, \tag{2}$$

where p is a constant less than one. This equation, which is empirical, was proposed by Rothmund and Kornfeld (63) because of its analogy with the Freundlich adsorption isotherm.

Rothmund and Kornfeld's equation is sometimes inconvenient because of the need for knowing the total amount of exchangeable ions in the solid. Another equation was proposed by Wiegner and Jenny (40):

$$y = K\cdot\left(\frac{c}{a-c}\right)^{p}; \tag{3}$$

y is the amount of exchange per gram of solid, c is the equivalent concentration of the added ions remaining in solution at equilibrium, and a is the equivalent concentration of these ions before exchange takes place.

Another equation (41) was proposed by Vageler and is similar to the Langmuir adsorption isotherm:

$$y = \frac{aS}{a + C}, \tag{4}$$

where y is the amount of exchange, a is the amount of ions added, S is the maximum exchange capacity of the solid, and C is a constant. Quantities of ions are expressed in equivalents per gram of solid.

The foregoing equations are all empirical and approximate. An equation which is not empirical, and which expresses very well the exchange equilibria on the surface of clay particles, was derived by Jenny (42). He calculated the distribution that would result when ions of one kind were brought into contact with ions of a second kind adsorbed on the surface of a colloidal particle, and took into account the oscillation volumes of both kinds of ions in the adsorbed layer. The greater the oscillation volume, the more easily is the ion displaced from the surface. The equation is:

$$w = \frac{(s + N) \pm \sqrt{(s + N)^2 - 4sN(1 - V_w/V_b)}}{2(1 - V_w/V_b)}. \tag{5}$$

The exchanger originally carries only ions of type "b," while the solution with which it is brought into contact contains only ions of type "w." Then,

w = number of ions adsorbed of species "w,"
s = saturation capacity of exchanger,
N = number of ions added in the solution,
V_w = oscillation volume of ions of type "w,"
V_b = oscillation volume of ions of type "b."

This equation has the theoretical drawback that the ionic "oscillation volumes" have to be chosen to fit the equation and do not correspond to any other measured quantities. It has the practical limitation that it does not work very well for synthetic aluminosilicates, which is to be expected, since the derivation considers the ions to be held on an exposed surface and not in the internal channels of a gel.

In the experience of the writer, the equation (2) of Rothmund and Kornfeld is as generally satisfactory as any in expressing ion exchange distributions. Typical published data on clays, glauconite, synthetic exchangers, and casein (7, 27, 40, 41, 55, 61) have been replotted according to this equation, and good agreement was found in every case. The constants K and p so derived are given in Table 3 below.

It is doubtful whether we can ascribe much theoretical significance to the Rothmund-Kornfeld equation, since it may not represent true equilibrium. It is interesting that in two of the rare cases where the same distribution of ions was reached from both sides, the simple law of mass action was obeyed (4, 50). If, however, the Rothmund-Kornfeld equation does represent a true equilibrium, it implies that the activity of each ion in the exchanger is proportional to a power of its concentration greater than one, and yet is almost unaffected by the concentration of the other ions in the exchanger. This is conceivable, because the energy of binding of an ion is probably not uniform throughout the solid, and different ions may find their lowest potential energy in different positions in the exchanger.

Ions of Different Valencies: Effect of Dilution.

In exchanges between ions of equal valency, the ratio of concentrations of ions in the exchanger depends only on the *ratio* of the concentrations in the solution, not on the total concentration. In exchanges between ions of different valencies, this is not so. The proportion of the ion of higher valency in the exchanger is greater, the more dilute the solution. An example of such an effect is seen in Table 2.

TABLE 2.

1 m. eq. Na^+ in exchanger plus 1.2 m. eq. $Ca(NO_3)_2$ in solution.

Concentration of Solution	Exchange Per Cent of Na^+ at 9° C.	at 21° C.
0.25N	42	50
0.1N	52	57
0.02N	66	67
0.005N	74	75
0.001N	—	80

Results of Patton and Ferguson (55), for gel type aluminosilicate.

These data and similar data of Rothmund and Kornfeld (63) are consistent with an equation

$$\left(\frac{c_{\mathrm{Ca}^{++}}}{c_{\mathrm{Na}^{+2}}}\right)_{\text{solid}} = K \cdot \left(\frac{a_{\mathrm{Ca}^{++}}}{a_{\mathrm{Na}^{+2}}}\right)^{p}_{\text{solution}}, \tag{6}$$

where $a_{\mathrm{Ca}^{++}}$, $a_{\mathrm{Na}^{+}}$ are activities. This is analogous to the mass action equation for equilibrium between univalent and divalent ions. Other data on the effect of dilution on the distribution do not fit this equation as well, however. Renold (61) found that below $0.1N$ the $\mathrm{Ca}^{++} : K^{+}$ ratios in an exchanger and a solution in contact with it were unaffected by dilution, while Patton and Ferguson (55) found that the effect of dilution on the barium-sodium exchange was less than would be expected from equation 6.

Effect of Temperature.

An example of the effect of temperature on ion exchange is seen in Table 2. Increase in temperature causes calcium, the ion of higher valency, to pass into the exchanger, the effect being greater, the higher the concentration. The data published are too few, however, to make any generalizations. In exchanges between ions of equal valency, temperature seems to have no effect (21, 63).

Distribution Constants of Different Cations.

A few sample values of K and p in the Rothmund-Kornfeld equation (Eq. 2, page 20) were calculated by the writer from published data and are set out in Table 3. The equation containing the first power of both ions' concentrations in solution was used even for exchanges between ions of different valencies, since it gives a good plot.

From this Table, it can be seen that the higher the atomic weight of an ion, the more firmly it is held by the exchanger; that is, the higher is K. Generally, K follows the lyotropic series for cations:

$$\mathrm{Li}^{+} < \mathrm{Na}^{+} < K^{+}, \mathrm{NH}_4^{+} < \mathrm{Rb}^{+} < \mathrm{Cs}^{+},$$

and

$$\mathrm{Mg}^{++} < \mathrm{Ca}^{++} < \mathrm{Sr}^{++} < \mathrm{Ba}^{++} < \mathrm{La}^{+++}.$$

Whether a given divalent ion, say, calcium, will be absorbed more or less strongly than, say, rubidium, depends on the concentration in solution and on the kind of exchanger, but, in general, divalent ions are absorbed more strongly than univalent, and trivalent more strongly than divalent. Hydrogen ion is an exception, being as strongly absorbed as barium, or more so. The heavy metals are strongly absorbed too, but among them there is no special order (61).

TABLE 3.

Constants in the Equation $\left(\frac{c_1}{c_2}\right)_{\text{solid}} = K\left(\frac{c_1}{c_2}\right)^{p}_{\text{solution}}$.

Exchange.	Reference.	p.	K.	Concentration.
NH_4X (fusion) + Na^+	40	0.67	0.35	
NH_4X (fusion) + K^+	40	0.72	1.0	
AgX (fusion) + Li^+	63	0.69	0.0062	
AgX (fusion) + K^+	63	0.46	0.122	
AgX (fusion) + Tl^+	63	0.50	0.59	
Li-bentonite + NH_4^+	41	0.8	1.25	
K-bentonite + NH_4^+	41	1.1	0.5	
NaX (gel) + Ca^{++}	55	0.63	0.67	0.25*N*
NaX (gel) + Ba^{++}	55	0.55	1.78	0.25*N*
NH_4X (fusion) + Ca^{++}	40	0.26	0.95	0.02–1.0*N*
NH_4X (fusion) + Mg^{++}	40	0.17	0.37	0.02–1.0*N*
K-greensand + Ca^{++}	7	0.6	0.6	1*N*
CaX (fusion) + Na^+	40	0.90	0.04	
CaX (fusion) + K^+	40	0.76	0.09	
CaX (gel) + Na^+	55	0.72	0.21	0.25*N*
Ba-casein + Na^+	27	0.7	0.0045	0.08*N*
Ca-casein + Ba^{++}	27	0.75	1.2	
Ba-casein + Ca^{++}	27	0.45	0.6	

Notes: (*a*) Ion "1" in the equation is the ion added in the solution; ion "2" is that originally present in the exchanger.

(*b*) The symbol "X" means synthetic aluminosilicate.

(*c*) The data on casein were plotted for constant swelling (see page 325).

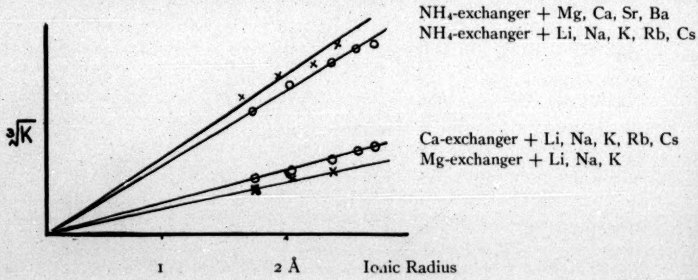
The correspondence of *K* with the lyotropic series suggests that the more hydrated an ion of given valency is in solution, the less strongly it is bound by an exchanger. This idea is substantiated by results of Wiegner (77, 78), who compared the displacing powers of solutions of caesium and sodium chlorides in different alcohol-water mixtures. As the proportion of alcohol was increased, and the hydration in solution correspondingly reduced, sodium and caesium became more nearly alike in their displacing power:

TABLE 5.

1 gram calcium aluminosilicate plus 3.45 m. eq. sodium chloride or caesium chloride.

Alcohol Per Cent.	Exchange m. eq. Na$^+$	Cs$^+$
0	0.64	0.98
40	0.99	1.10
100	1.23	1.25

The degree of hydration of an ion decreases with increasing ionic radius, and so does the exchanging power. A striking correlation was shown by Jenny (40), who plotted the ionic radius (found from crystal lattice measurements) against the cube root of *K* as given by his equation (Equation 3, page 21). The following graph was obtained:



The index *p* in Equation 2 seems to change at random from ion to ion. Jenny (40) found that the values of *p* in his own equation (Equation 3) fell into groups according to the valencies of the exchanging ions, but his figures are of doubtful significance because the concentration was continuously varying in his experiments.

A number of physical properties of cation exchangers are related to the exchangeable cation they carry through the lyotropic series; for example, the electrokinetic potential (75, 76), and the viscosity, swelling, and water absorption of clays (35, 77).

Effect of Swelling.

Owing to the increasing use of organic synthetic resins and treated coals as cation exchangers, the effect on their ion exchange properties of the swelling which these materials undergo when placed in water is of interest. No experimental data on swelling carbonaceous media are yet available, save for Graf's study of base exchange between casein and aqueous-alcoholic solutions (27). The swelling of casein was altered in three ways: (*a*) it was increased by increasing the salt content of the solution, (*b*) it was decreased by increasing the alcohol-water ratio in the solvent, (*c*) it was decreased by forming a resin of the casein with formaldehyde. In each case, increase of swelling increased considerably the exchange between barium casein and alkali and alkaline earth metal ions, and vice versa; or, swelling tended to make the affinity of casein for different ions more equal.

Because of the large effect of swelling on cation exchange, ion concentration-exchange relations must be expressed for a constant swelling in order to be significant. This was done by the writer in calculating the constants for the barium-sodium exchange in Table 3, but was not done by Graf in his paper.

Effect of Anions in Solution.

Patton and Ferguson (55) found that a sodium exchanger took up the same amount of calcium from calcium acetate solutions as from calcium nitrate solutions, indicating that the nature of the anion had no effect on cation exchange equilibria. The results of Raman and Spengel (60) are similar. A different conclusion was reached by Ungerer (70), who studied the exchange of calcium aluminosilicate with several different potassium salts and also with different salts of other cations. He found that in every case the nature of the anion affected the exchange, the exchange increasing in the order

$$\mathrm{CNS^- < IO_3^- < I^- < ClO_3^- < NO_3^- < Cl^- < SO_4^{=} < CrO_4^{=} < OAc^- < Fe(CN)_6^{\equiv}}.$$

The exchange was greater, the more hydrated the anion, and the effect of the anion was greater, the more hydrated the cation. Potassium acetate gave seventeen per cent.

more exchange than potassium chloride. The effect was found even in $N/100$ solutions, and was ascribed to the dehydration of the dissolved cations by the anions. A similar effect of anions was found in the displacement of hydrogen ions from peat by sodium salts. These results are in harmony with the view that the relative exchange powers of different cations are largely governed by their affinities for the solvent.

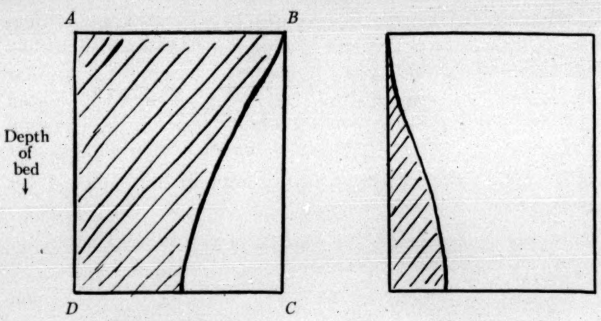
PART III.

TECHNICAL APPLICATIONS OF ION EXCHANGE.

Applications to Water Softening: Efficiency of a Softening Cycle.

By far the most important practical application of ion exchange is in water softening. Hard water, which contains calcium and magnesium salts, is passed through a bed of a material containing exchangeable sodium ions, when the calcium and magnesium ions are taken up by the exchanger and replaced by sodium. When the bed has lost so much sodium that the effluent from the bed is no longer soft, concentrated brine is passed; the adsorbed calcium and magnesium are displaced again by sodium, and the bed is ready to soften another quantity of water.

It is obvious that in such a cycle the calcium and magnesium which are taken up by the bed are only a fraction of the maximum that the exchanger can hold. The softening run is stopped as soon as the effluent contains appreciable quantities of calcium or magnesium. At this stage, the layer of exchanger which is nearest the outlet of the softening chamber contains only a small fraction of these ions, most of it being still in the sodium condition. The proportion of calcium or magnesium will increase as one proceeds towards the inlet of the chamber, the layer nearest the inlet being practically saturated with the divalent ions. Again, on regeneration, the quantity of salt passed is not sufficient to displace all the calcium and magnesium; for this would require a large excess. Consequently, after regeneration, some divalent ions still remain in the softener, being located mainly in the lower half of the bed (assuming downward flow). The distribution of ions in the bed of exchanger can be represented graphically as follows (7):



At end of softening run

After regeneration

The difference in the areas of the two shaded portions represents the "operating capacity" of the bed (68).

The "operating capacity" depends upon several factors besides the maximum exchange capacity of the bed (represented by the whole rectangle *ABCD* in the above graphs). It depends upon the rate of reaction between the exchanger and the solution, and on the equilibrium distribution of ions between the exchanger and the solution. The latter we can treat theoretically in a semi-quantitative manner by applying the Rothmund-Kornfeld equation. Let us consider a hard water containing calcium as the only cation, passing over a bed of exchanger containing only sodium as the replaceable cation, and let us further assume that the flow rate is slow enough that a distribution corresponding to the Rothmund-Kornfeld equation is set up.

The efficiency with which the total capacity of the bed can be used for taking up calcium ions will be governed mainly by the amount of calcium ions that the bottom layers of the bed can hold and still let pass an effluent which is practically free from calcium. Generally, the softening run is stopped when the calcium in the effluent reaches 0.1–0.2 m. eq. per liter. Let us assume that at this point the Ca : Na ratio is 1:50 or 0.02.

The data of Patton and Ferguson (55) for sodium aluminosilicate plus $N/1000$ calcium ions give a Rothmund-Kornfeld equation as follows:

$$\left(\frac{\text{Ca}}{\text{Na}}\right)_{\text{exchanger}} = 4.8\left(\frac{\text{Ca}}{\text{Na}}\right)^{0.4}_{\text{solution}}.$$

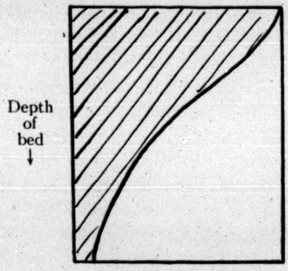
At the end of the softening run we have in the bottom layer of the bed,

$$\begin{aligned}\left(\frac{\text{Ca}}{\text{Na}}\right)_{\text{exchanger}} &= 4.8\ (0.02)^{0.4}\\ &= 4.8\cdot 0.23\\ &= \mathit{1.10}\end{aligned}$$

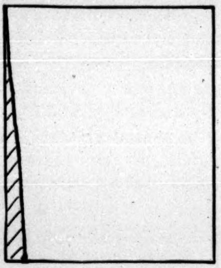
or fifty-five times the Ca : Na ratio in the water. If a higher Ca : Na ratio can be tolerated in the effluent, as will be the case for an influent water of lower calcium content, the ratio in the exchanger will be even higher.

The constants in the Rothmund-Kornfeld equation are very favorable to efficient operation in this particular case; for a large proportion of the lower layers of the bed can be occupied by calcium ions and still give an effluent containing almost no calcium. Moreover, the effect of concentration on the Ca-Na distribution favors efficient regeneration in this softening cycle, because in concentrated solutions, such as are used in regeneration, the distribution shifts, making calcium ion less strongly absorbed by the exchanger.

The distribution of ions between exchanger and solution is not always so favorable to efficient operation as in the case just considered. For example, when water containing calcium and sodium ions is passed over a carbonaceous exchanger containing replaceable hydrogen ions, the hydrogen ion is bound by the exchanger about as strongly as calcium and more strongly than sodium (i.e., K in the above equation is one or less), so that sodium and calcium start to appear in the effluent before the bottom layer of exchanger has taken up more than a small proportion of these ions. The distribution of ions in the bed will look something like this:



Fraction of Ca^{++} →
At end of softening run



After regeneration

In this case, the regeneration process will be more efficient, but the net result is likely to be that the proportion of the total exchange capacity which can actually be used under normal operating conditions is less than in the replacement of calcium by sodium. In practice, the operating capacity of carbonaceous exchangers on the H^{+}-Ca^{++} cycle is less than that on the Na^{+}-Ca^{++} cycle.

It is easy to see that the capacity will be lower for a hard water containing magnesium than for one which contains only calcium, because magnesium is less strongly bound by an exchanger than is calcium (see Part II of this paper). The presence of sodium ions in the influent water will lower the capacity, too, both in treating with a hydrogen exchanger and in softening with a sodium exchanger. The hardness of the influent water will affect the capacity; for the less calcium (or magnesium) that it contains, the higher is the effluent Ca : Na ratio (or Ca : H, or Mg : Na, or Mg : H) that can be tolerated, and the higher is the capacity. Moreover, lowering the electrolyte concentration shifts the Ca-Na equilibrium to favor the intake of calcium by the bed, so that again a low hardness favors a high capacity. The shift of the Ca : Na equilibrium with concentration means, too, that in the regeneration step a sodium chloride solution of high concentration will extract the calcium more efficiently than the same amount of sodium chloride present in more dilute solution.

The rate of reaction of the exchanger with the influent and with the regenerant is almost as important in determining the operating capacity as are the equilibrium conditions. The reaction rate depends on the nature of the exchanger and on the size and shape of its granules, and on the flow rate. Up to a point, the slower is the flow rate of the influent or regenerant, the higher is the capacity; but, if the flow rate is reduced below a certain point, the liquid can slip past the granules without actually coming into contact with them, and so can escape reaction. Above this critical flow rate, the flow is turbulent and all the liquid has a chance to touch the granules. There is thus no advantage in using excessively slow regeneration rates. For this reason, too, the concentration of regenerant which can be employed advantageously is limited; for a very concentrated regenerating brine must of necessity flow very slowly to give time for complete reaction. In practice, the optimum sodium chloride concentration is found to be about six per cent.

The efficiency of distribution of the influent and, especially, the regenerant, is a factor in large units, where there is a danger that the granules near the circumference of the bed will not receive their full share of the total flow. This danger can be minimized by good softener design, but it too sets limits on the flow rate and the volume of regenerant.

Total Removal of Electrolytes from Water.

So long as the cations of hard water could be replaced only by other metallic cations, such as sodium ion, the total electrolyte content of water could never be reduced by cation exchange. Carbonaceous exchangers, however, make it possible to replace metallic cations by hydrogen ions, and so open the way to the complete removal of electrolytes from water.

If a natural water containing only bicarbonates is passed over an exchanger saturated with hydrogen ions, the effluent contains only carbonic acid in solution, which can be removed by aeration, leaving pure water (6). If the raw water also contains chlorides or sulfates, these ions will, of course, remain behind as hydrochloric or sulfuric acid. This acid can be neutralized if desired by passing a portion of the raw water through a sodium exchanger and adding the resulting sodium bicarbonate solution to the acid effluent, or it can be removed completely by passing the water through a bed of acid absorbing material such as aniline black or metaphenylene diamineformaldehyde resin. This second bed can be regenerated with sodium carbonate or other alkali. The effluent from this bed is practically pure water, and the cost of such purification is less than that of distilling the water, provided the electrolyte concentration was not too large. This two-step proces is called "De-Mineralizing" (1, 43).

Special Applications in Water Treatment.

It is sometimes desirable to remove small quantities of a specific impurity from water even though complete electrolyte removal or softening may not be necessary. We have already reviewed one such instance; namely, the removal of traces of fluoride by means of anion exchange with basic tricalcium phosphate (page 312). A similar example is the use of cation exchange to remove small amounts of heavy metals from drinking water. Most heavy metals, such as copper and lead are absorbed strongly by an exchanger, even when the latter is saturated with calcium from a hard water. Traces of iron and manganese can be removed in the same way, but are removed more efficiently by oxidation with an activated oxide of manganese supported on a cation exchanger as a carrier. The exchanger is first saturated with manganous ion, and then sodium permanganate solution is passed; the manganous ion reacts with permanganate to form a high oxide of manganese, while the sodium ion takes its place as the cation in the exchanger. When water containing ferrous or manganous salts is now passed through the bed, the iron and manganese are precipitated out as ferric oxide and manganese dioxide. The bed can be regenerated by permanganate solution (5).

Ion Exchange Applications Outside Water Treatment.

One of the first applications of synthetic cation exchangers was in the purification of sugar juices. The juices were passed over a calcium exchanger, when the potassium and sodium ions in solution were replaced by calcium. The resulting solution crystallized more readily and completely than the untreated juice to give a sugar of lower ash content

(18). Cation exchangers can be used to remove lead from maple syrup (79), or heavy metals from sugar juices (52).

Ion exchangers may similarly be used for the recovery or concentration of valuable substances present as ions in solution in small amounts. Thus, copper can be recovered from rayon spinning waste liquors, which contain copper-ammonia complex ions (37). The copper is taken up first as $Cu(NH_3)_4^{++}$, then as the ion $Cu(NH_3)_2^{++}$. Metals can be recovered in a similar manner from electroplating wastes. In such applications, carbonaceous exchangers have decided advantages over siliceous exchangers, as they can be regenerated with acid and used in solutions of low pH. Organic bases, such as alkaloids (28, 69), and even amino-acids (62) can be recovered from solutions in the same way.

An unusual application of cation exchangers is in the separation of isotopes. When solutions of lithium, potassium, and ammonium salts were percolated through a long bed of exchanger, the isotopic ratio in the cations leaving the bed was found to be shifted, showing that preferential exchange of one of the isotopes was taking place. In each case, the rarer isotope was taken up preferentially by the bed (19).

Ion exchange has been applied in analysis to separate anions from cations, which may then be determined separately (64*a*). A very good method for the determination of ammonia nitrogen in urine depends on absorption of ammonium ions in an exchanger which contains replaceable hydrogen ions, then subsequently liberating the ammonia with alkali and estimating it colorimetrically (22).

Carbonaceous exchangers containing exchangeable hydrogen ions can be used to promote acid-catalyzed reactions such as the hydrolysis of starch to glucose (53), and have the advantage over sulfuric acid, which is normally used to catalyze such reactions, that the resulting glucose solution can be concentrated and crystallized more easily. Exchangers which are partially saturated with hydrogen ion serve as solid buffers for controlling the pH of solutions. This is desirable in fermentation industries, such as the production of lactic acid from sugars (28). Not only hydrogen ion, but any cation, can be buffered in a similar way. An example is the "buffering" of calcium and sodium ions in milk. The ratio of calcium to sodium in cow's milk is greater than that in human milk, but it can be made equal to the ratio in human milk by passing the milk over an exchanger containing calcium and sodium ions in the right proportion (44).

Ion exchange may be used as a method for preparing salts. It has actually been employed in Norway for making sodium nitrate from calcium nitrate and sea water. The exchanger is saturated with sodium by passing sea water, and then calcium nitrate solution is passed (54). A combination of favorable circumstances makes the method economical in this particular case, but, in general, the use of ion exchange for preparing salts is limited because transformations are not complete enough or cannot be carried out in concentrated solutions because of the insufficient capacity of available exchangers.

Any number of applications for ion exchangers can be devised along the lines of the foregoing. Relatively few of the many possibilities have been exploited, largely because the same end has hitherto been achieved more economically or more efficiently by other means, but the introduction of carbonaceous exchangers with their peculiar advantages is likely to create a vast field of commercial applications of ion exchange reactions.

Materials Made from Ion Exchangers.

In all the applications discussed so far, the usefulness of the exchanger has consisted solely in its cation exchanging property. The materials themselves can, however, be processed in some cases to yield useful products. The synthetic aluminosilicates can be converted into colored bodies very similar to the ultramarines by digesting them with alkali sulfide solutions, the color depending upon the cation originally present in the aluminosilicates, being blue for sodium, violet for zinc, orange for cadmium, grey for manganese, etc. (62). The same colored ultramarines may be obtained from natural ultramarine by cation exchange (49).

Natural and artificial aluminosilicate exchangers are used as dehydrating agents in the production of hydrocyanic acid from formamide (32). They can be used for making catalysts by introducing an appropriate metallic ion (62). The "vanadium zeolite" made from an exchanger and a vanadium salt is probably of this type; it is a catalyst for certain organic oxidations; for example, the oxidation of naphthalene to phthalic anhydride (39, 62). A vanadium complex silicate has been proposed as a catalyst in sulfuric acid manufacture, but this is not prepared by cation exchange.

Cation exchange in bentonite is used to make "Alsifilm," a substitue for mica, which has been termed "the first inorganic plastic." A bentonite sol, when allowed to evaporate on a plate, leaves a coherent paper-like film which, however, swells and disperses in water just like the original clay. If the exchangeable sodium of the bentonite is first replaced by potassium, and the film formed is dried at 110°, it is quite resistent to water. The reason is that the potassium ion is too large to enter the interior planal channel of the montmorillonite crystal (see page 308), but fits *between* adjacent crystal units and holds them together electrostatically, thus preventing swelling and dispersion (31).

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Battelle Memorial Institute Will Make Large Expansion. (*Blast Furnace and Steel Plant*, Vol. 29, No. 8.)—A fourth major building program in recent years is under way at Battelle Memorial Institute, Columbus, Ohio, where a 160,000-dollar addition to the process metallurgy laboratory building is under construction, Clyde E. Williams, Institute director, has announced. Additional space demands of enlarged research programs concerned with the study of chemical and metallurgical processes on a pilot-plant scale will be provided for when the new structure is completed. The expansion is the result of a continued increase in the Institute's research for industry, particularly in the fields of coal preparation, raw materials beneficiation, hydrometallurgy, pyrometallurgy, electrometallurgy, and foundry practice. Because of current world conditions and the resultant emphasis on the development and utilization of domestic raw materials and substitute materials, research by American industry has greatly increased, Mr. Williams stated. Current research investigations at Battelle are instituted partly by industries closely associated with the defense program and partly by those industries that are anticipating the adjustments of the post-emergency period with new and improved products and reduced production costs. The new structure will be 70 feet by 105 feet in plan, with five full floors, and will provide 35,000 square feet of additional space. Its steel, brick, and concrete construction will conform with that of the other Institute buildings. Office-laboratory facilities are planned for fifty additional research engineers and technicians. The new laboratories will be equipped with the most modern facilities. To handle the equipment necessary for pilot-plant operations, provision has been made for high floor loads and the necessary crane service. This is the fourth time in recent years that space requirements have led to laboratory expansion. Just a few months ago, eighteen new laboratories and offices, totaling nearly 10,000 square feet, were installed. The majority of these laboratories are in the new laboratory building which was completed only a year ago. The process metallurgy laboratory building, to which the present construction is an addition, was completed in 1937. Battelle Memorial Institute is one of the country's larger industrial research organizations. It was established and endowed by the wills of Gordon Battelle and his mother, Annie Norton Battelle, to encourage and conduct scientific research for industry and to further research education. It carries on fundamental and applied research in ferrous and non-ferrous metallurgy, ceramics, physics, organic or inorganic chemistry, fuels, coal preparation and utilization, ore-dressing, and materials concentration. Research is done both with its own funds and for industrial sponsors.

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THE RADIOSONDE: THE STRATOSPHERE LABORATORY.

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(*Continued from September issue.*)

3. Balloon Technique.*

A large part of the present-day physical technique of ballooning was developed by early meteorologists [15] who sent recording instruments and pilot balloons to the stratosphere, and this part of radiometeorography represents the result of many years' experience. We shall review briefly a few of the more important considerations and methods.

The chief requirements in the choice of a location from which to operate are first that it be near the receiving station, so that it may be ascertained just before take-off whether signals are being heard satisfactorily, and second that the surrounding geography be such that the flight will clear all obstacles in rising from the ground, no matter in which direction the wind may be blowing. Accordingly, for flights other than meteorological, open fields or flat rooftops (Fig. 10) are ideal. When the flight must be launched in all kinds of weather, a protected location is needed, such that with a strong wind blowing, the balloons can be inflated without difficulty and yet have time to clear the surroundings. Some weather stations employ a "balloon howitzer," a topless box large enough to hold the balloon during inflation until the moment of take-off when it rises out of the box.

Meteorological flights rarely require more than one balloon, since the weight of the instrument is usually less than a

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* For altitude-pressure tables based on the U. S. Standard Atmosphere, see N.A.C.A. Report No. 538, for sale by Government Printing Office, Supt. Documents, Washington, D. C., 5 cents.

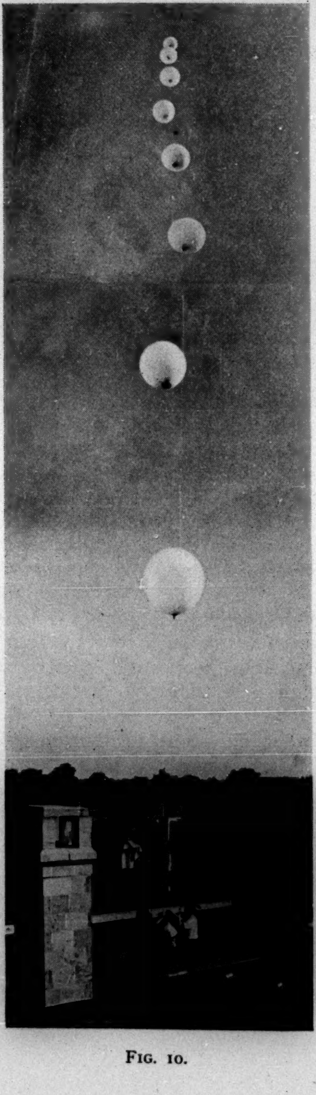

FIG. 10.

kilogram. Ascensions for other purposes, for instance for the study of electrical phenomena or cosmic rays, ordinarily weigh much more, and so must use several balloons. In either case, by far the best balloon has been found to be the latex rubber type (700 grams),* inflated with hydrogen to a diameter of about 5 feet and tied off so as to retain its filling. As it rises into regions of lower pressure it will expand. Its bursting diameter is about 20 feet, which it will reach at some 25 kilometers altitude. This diameter is not definite, but depends both on the individual balloon and on the amount of local heating, and consequent deterioration, which it has received from the sunlight during ascent. Experiments have also been made on cellophane balloons[16] constructed with open necks, but these were found not to be worth the added difficulties in building and launching them.

Since the bursting diameter of the latex balloons depends to a large extent upon the individual balloon, no exact calculations can be made predicting the maximum altitude which a flight will reach. However, the relationships between lifting force, balloon diameters, and altitude can easily be derived, and from these an estimate can be made of the maximum obtainable height if we assume a most probable bursting diameter.

Since the tied-off balloon contains a constant mass of hydrogen, we may write

$$L = \frac{4}{3}\pi r_s^3(\rho_a - \rho_H) \times 10^6 = 5000 \ r_s^3, \qquad (1)$$

where L is the total lift of the hydrogen in grams, r_s the sea level radius in meters, and ρ_a and ρ_H the densities of air and hydrogen at sea level. Now

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* Made by the Dewey & Almy Chemical Co., Cambridge, Massachusetts.

FIG. 10. An eight-balloon cosmic ray flight ready to be launched from the roof of the Bartol Foundation. The balloons are attached at intervals of about 25 feet along the rigging cord, which is fastened at its lower end to the flight set. The two observers are steadying the cosmic ray counter instrument wrapped in its cellophane jacket, while above them are attached the finder's return postcard and the radio transmitter. The antenna extends upward along the balloon cord above the transmitter. This flight weighed 15 pounds, and attained an altitude of 80,000 feet. It landed about three hours later at a point 32 miles away. The long string of balloons, most of which are still intact upon landing, serve to attract attention to the apparatus.

$$\frac{r_s^3}{r_b^3} = \frac{P_b}{P_s}, \tag{2}$$

where r_b is the bursting radius in meters occurring at a pressure P_b, and P_s is the atmospheric pressure at sea level. Combining these, we find that

$$L = F + w + W = 5000 \quad r_b^3(P_b/P_s), \tag{3}$$

where F is the free lift of the balloon of weight w carrying a load of W grams. Now w, W, and P_s are known, while a reasonable value may be given for r_b, and hence we have a relation between the maximum altitude P_b in terms of the

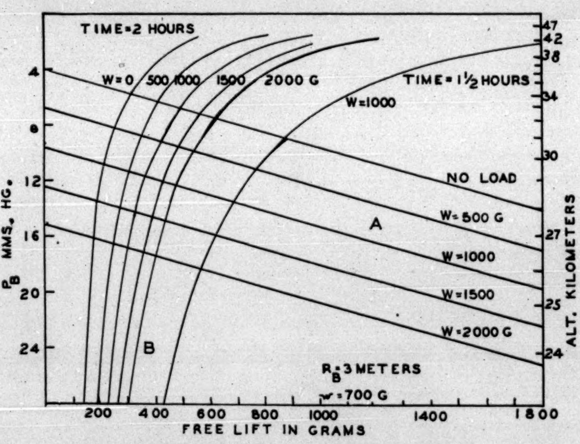

FIG. 11. Maximum altitude in mm Hg as a function of free lift for various loads per balloon, assuming the weight of the balloon fabric w to be 700 grams, and a bursting diameter of 6 meters. Curves A give the maximum possible altitudes for any rate of rise, while curves B represent the altitudes attained with various loads and times after take-off. The intersections of corresponding curves A and B indicate optimum free lifts to minimize the effects of deterioration on the balloons and thus allow attainment of highest altitudes. Free lifts less than these values will yield altitudes limited by curves B, while lifts greater than these will give altitudes determined by the curves A.

free lift F. A family of curves, A, corresponding to various values of W are given in Fig. 11, assuming typical values for w and r_b. It will be seen that, due to the weight of the balloon fabric, definite maxima are set on the possible altitudes, and that these maxima decline with increasing free lift. Thus the greatest heights should be obtained when the free lift is at a minimum, i.e., when the rate of ascent is very low.

Many observers, however, have reported that flights using high ascensional velocities had reached greater elevations than other similar flights rising more slowly. This contradiction to the derivation just made may be accounted for by the effects of deterioration of the balloons during flight. Very little is known concerning this phenomenon except that it appears to be a function of time. Let us assume, therefore, that the flight must reach its maximum altitude within a given time after takeoff, and thus set a lower limit to the rate of ascent. In order to include this limit in Fig. 11, we must express it as a function of free lift. To do this, we use the familiar law of motion of a body in a turbulent fluid,

$$F = (k/g)\rho_a v^2 A, \tag{4}$$

where F is the retarding force in grams, k a dimensionless constant depending on the geometrical shape of the body and on the Reynold's Number, g the acceleration of gravity, ρ_a the density of the fluid in grams/cc, v the velocity in cm/sec, and A the cross-sectional area in cm^2 of the body normal to the direction of flow. The effects of viscous (streamline) forces and of pressure created by the elastic contraction of the rubber balloon fabric can both be shown to be small and may be neglected. It is also evident that the retarding force is equal to the free lift, and hence

$$F = V(\rho_a - \rho_H) - (w + W), \tag{5}$$

where V is the volume of the balloon, ρ_a and ρ_H the densities of air and hydrogen respectively, w the weight of the balloon fabric and W the load, both in grams.

Since $A = \pi r^2$, and $V = \dfrac{4}{3}\pi r^3$, where r is the radius of the balloon, we can rewrite equations (4) and (5), and combine them:

$$v^2 = \frac{4}{3} g \left(\frac{\rho_a - \rho_H}{\rho_a} \right) \left(\frac{F}{F + w + W} \right) \frac{r}{k}. \tag{6}$$

From equation (5) we get

$$V = \frac{F + w + W}{\rho_a - \rho_H} = \frac{4}{3} \pi r^3,$$

and thus

$$r = \left(\frac{3}{4\pi} \frac{F + w + W}{\rho_a - \rho_H} \right)^{1/3}. \tag{7}$$

Replacing r in equation (6) by equation (7) and taking the square root, we obtain finally

$$v = \left(\frac{4}{3} \left[1 - \frac{\rho_H}{\rho_a} \right] \right)^{1/3} \frac{g^{1/2}}{[\pi(\rho_a - \rho_H)]^{1/6}} \left(\frac{F}{R} \right)^{1/2} \frac{1}{(F + w + W)^{1/3}}$$

$$= 272 \frac{F^{1/2}}{(F + w + W)^{1/3}} \text{ cm/sec at sea level.}$$

Since it is an experimental fact that these balloons rise at a constant rate at all observable altitudes, a phenomenon which will be discussed below, we may use this formula connecting rate of rise with free lift in Fig. 11, curves *B*. These represent altitudes attained at various times after takeoff as functions of free lift and load. The optimum free lift is then that at which the proper one of the curves *B* intersects the corresponding curve of the family *A* for a given load. In the event that several balloons are used, the figures represent the values per balloon.

Values of the resistance coefficient k depend on the shape of the body, in this case a sphere, and on the Reynold's Number $R = vr/\nu$, where ν is the kinematic viscosity (viscosity/density). For the usual size and rate of rise of radiosonde balloons (350 or 700 grams, rising at about 4 meters per second), the Reynold's Number at sea level [17a] is about 2×10^5, decreasing to 5×10^4 at a pressure of 4 cms. Hg. Fig. 12 shows the experimental relation between R and k in the range under consideration, and it may be seen that values of R greater than 10^5 yield $k = 0.10$, while those between 10^5

and 10^3 correspond to $k = 0.25$, the large variation being caused by an abrupt change in the type of fluid resistance at $R = 10^5$. But this increase of k with elevation corresponds almost exactly with the increase in the radius r, with the result that r/k is constant and hence (see equation (6)) the rate of rise of these balloons is independent of altitude.

It is apparent that if balloons are described at sea level by a Reynold's Number less than 10^5 or greater than 10^6, they will not exhibit a constant rate of rise but will increase in speed as they ascend. The Reynold's Number decreases by about a factor of 4 with elevation to 4 cms Hg, and inspection of Fig. 12 shows that in the domains just given, k will remain constant throughout the flight. Accordingly, equation (6) predicts that v will be proportional to $r^{1/2}$. Thus the balloons

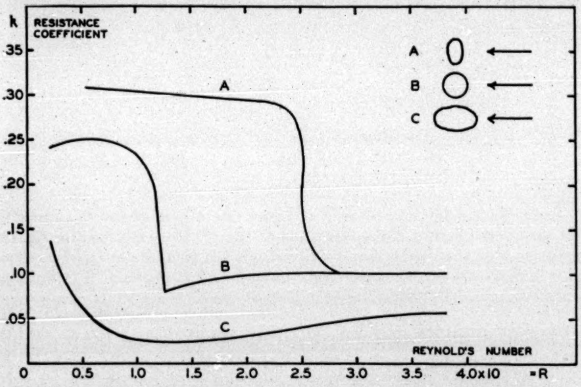

FIG. 12. Variation of resistance coefficient k with Reynold's Number $R = vr/\nu$, for a sphere (B) and for ellipsoids of revolution with their major axes parallel (C) and perpendicular (A) to the direction of motion through the air (from Reference 17*b*). Pilot balloons of the usual type and upward velocity begin at take-off with a Reynold's Number of about 1.5 to 2.0×10^5, which decreases by about a factor of 4 with elevation to 70,000 feet. Since the balloon is spherical, the resistance coefficient in this range varies rapidly and in such a manner as to cause the balloon to rise with a constant velocity. If the balloon is of appreciably different size or velocity the resistance coefficient will not vary in this way and the flight will ascend with increasing velocity as it attains higher altitudes.

of 30 cms radius reported by Frost[18] rose faster as they gained altitude since their Reynold's Number was of the order of 5×10^4 at sea level.

Table I gives a comparison between observed and calculated values of the rates of rise of several balloon flights made recently at the Bartol Research Foundation. It will be seen that balloons whose Reynold's Numbers lie in the neighborhood of 1.8×10^5 yield a calculated rate of rise equal to the average observed rate of rise over the total upward part of the flight, while if R is appreciably greater, the calculated velocity is lower than the observed. Thus the former travel upwards at a constant velocity, while the latter increase in speed with elevation.

TABLE I.

No. of Balloons.	Per Balloon.			Reynold's Number R $\times 10^{-5}$.	Calculated v cm/sec Sea Level.	Observed Average v cm/sec.
	F.	w grams.	W.			
6	170	350	680	1.6	335	355
6	280	350	610	1.9	425	410
8	330	350	870	2.0	425	400
8	190	350	710	1.6	340	335
6	330	700	1170	2.0	380	385
7	230	350	970	2.5	355	510

Table I. Comparison between observed rate of rise of balloons averaged over the upward portion of the flights and calculated values based on the derived formula. Note that flights described by Reynold's Numbers larger than about 2×10^5 show a larger observed velocity because of the increase in rate of rise with elevation. Balloons are far enough apart to avoid interaction.

Using a single balloon, the radiosonde must be provided with a parachute, but when several balloons are attached, in general not all of them will burst and the remaining ones will cause the flight slowly to return to earth. This slow rate of descent is desirable not only to prevent destruction of the apparatus on landing, but also because it permits the collection of further data during descent. In addition, when several balloons are used the lifting force of each can be set so that when the first one bursts, the total lift will exactly equal the weight and the instrument will float at a constant altitude. This arrangement is often of great advantage for certain types of observations. Several observers have reported flights

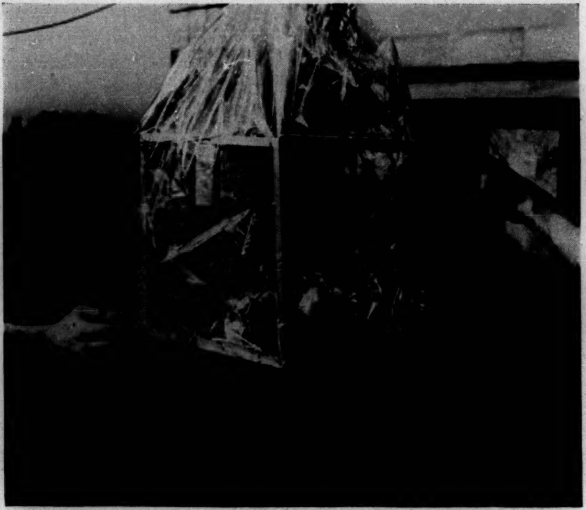

FIG. 13. Radio-cosmic-ray equipment ready for balloon flight. Cellophane cover keeps sun's heat inside by the "greenhouse" effect, while stratosphere temperatures outside may fall to − 60° C. Batteries, vacuum tubes of the control circuits and the cosmic-ray counter may be seen inside. This instrument measured several different counting rates, and is probably the first experiment with its own complete control-conditions to be made in the stratosphere. This instrument was recovered, and made three flights, one reaching 86,000 feet.

which "leveled off,"[24] one of the earliest and longest of which[19a,b] was launched from the Bartol on July 27, 1938 and remained in the air giving readable radio signals for 10½ hours. It leveled off at 66,000 feet and remained at this elevation for 7 hours. After this time, one of the remaining balloons burst and the flight returned to earth. It should be added that any flight which comes into equilibrium at any elevation and floats during the day would descend as soon as night fell and the solar heating effects on the balloon ceased.

When several balloons are used, it has been found best to harness them one above the other, spaced about 10 meters apart, in this way keeping them from contact with one another

(Fig. 10). Two or more balloons at the same level are very unstable aerodynamically, setting up low pressure regions between them in their upward passage through the air and causing them to oscillate violently. The rigging is made up of a central rope, from which short cords branch off at intervals to the balloons. At each branch point a releaser may be attached, consisting of a metal hook so designed that when that balloon bursts, the remains will detach themselves from the rigging and fall away. Such releasers were first reported by Korff [19a] in 1938 and have been used successfully by other observers [19b, c] also.

The radiosonde must be protected in some way from the intense cold which prevails in the stratosphere, since the batteries will not operate at temperatures below – 20° C. For daytime flights this is easily accomplished, following Regener's technique,[20] by enclosing the entire apparatus in a double layer of cellophane (Fig. 13), warming the interior by radiation in much the same way as a greenhouse. Ample heat is thus obtained; measurements have shown that the average temperature within is often 50° C. while that of the surrounding air is – 70° C. At night the radiosonde must be surrounded with very effective insulation to retain its heat as long as possible. Rock wool and kapok have been used to good effect. Heat may also be generated within the apparatus by allowing water to drop slowly on a supply of calcium oxide, though this procedure involves a large increase in weight. This arrangement has been used successfully at the Bartol Foundation in connection with some night flights [21c] in which it was desired to keep a fairly large apparatus warm.

4. Application to Cosmic Ray Studies.[21]

We shall consider one application of the radiosonde other than meteorological, that to cosmic ray work. Here the apparatus observes, beside pressure and temperature, some particular phase of the cosmic rays, employing either a Geiger-Mueller counter or an ionization chamber-electrometer combination to detect them. Electrometer flights are not often made, because of the great weight of the apparatus in its present state of development; Keen's flights,[22b] for instance, weighed 40 pounds. The counter, however, is admirably suited to this work, both because of its comparative lightness and because its data are in the form of electrical pulses which may be transmitted to the observer together with those of the Olland type barograph.

A Geiger counter is a device which produces a small voltage pulse when a cosmic ray or other ionizing particle passes through it. Counters of various types, operating for many special purposes, have been described in detail in the literature[26] and will not be reviewed here. In general, they are controlled by a simple resistance-coupled amplifying circuit, which renders the output pulse large enough to operate a relay keying the radiosonde transmitter. Moreover, since the counter produces a pulse of duration of about 10^{-4} second, and since it is desired to have the transmitted pulse be about 0.1 second in length in order to facilitate recording by a pen on tape, a pulse-delay circuit is included. Several types of pulse-prolonging circuits are possible, one of which being the "multivibrator" arrangement, developed for this purpose by Johnson and Korff[21b,d,19c] at the Bartol. The multivibrator is negatively biased so that it remains locked normally with

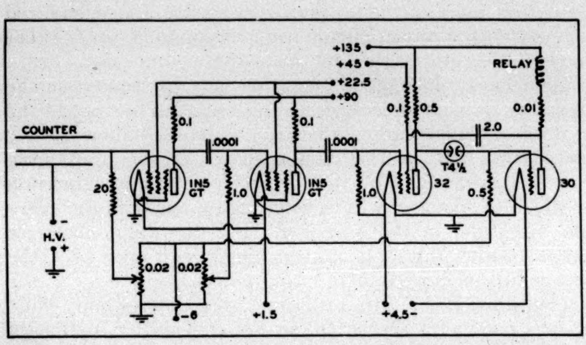

FIG. 14. Circuit used in radio transmission of cosmic-ray intensities. At the left, a cosmic-ray proportional counter. The two 1N5GT'S constitute a resistance-coupled pulse amplifier, the last two tubes a pulse-prolonging multivibrator, which keys the radio transmitter through the relay. Resistances are in megohms, capacitances in microfarads. The neon bulb (T4½) may be replaced by a capacitor.

one tube conducting and the other tube non-conducting, while upon the arrival of a pulse of sufficient amplitude on the grid of the first tube, the multivibrator circuit goes through one cycle and then locks again in the initial stable state. In this cycle, the amplitude and time-length of the pulse in the output tube are independent of the amplitude and length of the input pulse, but depend only on the voltage and electrical constants of the multivibrator circuit. That shown in Fig. 14 produces an output pulse of the order of two tenths of a second. By connecting the return circuit from the plate of the last tube to the screen grid of the first, instead of to the control grid as is customarily done, good operation may be secured and the necessity for high impedance arrangements to prevent the loss of the input pulse through the output circuit eliminated. The amplifying unit in the circuit shown is for proportional counters operating below the normal Geiger counter threshold, in which the counter wire is connected directly to the grid of the first tube in the amplifier. For operation above the Geiger counter threshold, a quenching circuit must be used [21b] or a self-quenching counter employed.

The pulse in the output tube operates a keying relay, which in turn completes the circuit in the transmitter, permitting the latter to oscillate. The keying relay contacts may be in parallel with those of the Olland type radiobarograph, and will thus secure the transmission of both the cosmic ray and the pressure data. No additional signal is sent out if the cosmic-ray contact closes while the barograph contact happens to be closed. Therefore if it is desired to make an absolute determination of the counting rate, it is necessary to allow for the fraction of the total time of one Olland cycle during which the transmitter is emitting the pressure, temperature, and reference signals. This fraction will ordinarily be of the order of ten per cent., and will of course be independent of altitude.

When a high counting rate is to be measured, as when using a large counter, it is desirable to employ a scaling circuit. Such a circuit will circumvent the necessity of measuring a large number of pulses, and will also avoid the limitation on the number and spacing of random counts due to the finite resolving time of the recorder which is usually the slowest part of the entire system. Such scaling circuits have been designed to be included in the apparatus carried by the balloon, by Johnson,[19c,21a] by Korff,[21c,25] and by Curtiss.[28] Alternatively the scaling circuit may be attached to the receiver. This arrangement has been used by Carmichael and Dymond.[21e] In the latter case, however, the high counting rate must be transmitted and the keying relay must be capable of quick recovery.

For keying relays, a high resistance telephone relay, such as the Western Electric Type G-26, operating on about two milliamperes, is satisfactory. Considerably lighter relays have also been constructed at the Bartol Foundation, using two telephone headset coils of 1000 ohms each and a light beryllium-copper spring armature to which a small piece of iron had been soldered. Platinum contact wires are attached to the end of the armature.

In cosmic-ray observations it is often desirable to make control experiments. In general this involves arranging the circuit which must measure the quantity under discussion and then change over to a standard or controlled condition, repeating this arrangement cyclically at a suitable interval.* This may be accomplished either by switching between the unknown and the control conditions, or by actually moving the position of the counter, through a cycle of positions. The techniques for both operations have been developed by Korff [25,27] and by Johnson.[19c] The latter caused a counter to occupy a position between two other counters, and then to be transported at right angles to its axis to a new position. In the first position the counter measured one quantity, in the second position another. The movement was accomplished by mounting the counter on a spring-controlled arm which had two stable positions. The arm was actuated by a crank driven at a slow speed by a small geared-down electric motor of the type used in the radiobarograph. The counter therefore remained in each position for a time of the order of a minute, and the counting rates in the two positions could be observed as a function of elevation.

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* Other types of control-observations have been developed by A. H. Compton and his collaborators, but since these are used in connection with recording instruments and not with radio-transmitted technique, they are not within the scope of this review.

In the other experiment cited,[25] a counter was caused to occupy four successive positions with respect to lead blocks, the counting rate in each position being the quantity to be measured at various elevations (see Fig. 13). This was done by mounting the counter on an arm, which was caused to rotate slowly by a small electric motor, and thus to be swung alternately near the lead blocks and far from them. This cycle was completed in four minutes, the counting rate being thus determined in each of the four positions during a one-minute period. Contacts between the moving counter and the stationary control circuit were maintained through brass slip-rings on each of which a multi-pronged beryllium-copper spring brush rubbed. Satisfactory positive non-interrupted contact with the moving units could thus be maintained.

In another type of control experiment,[27] where it was desired to measure two quantities alternately, but in which it was not necessary to move the counter, a microswitch was operated by a cam driven by a small motor. The motor was geared down to rotate the cam once in four minutes. The cam pressed against the actuating lever of the microswitch, so that the switch was open for approximately half the total time and closed for the balance. In this manner a sufficiently continuous measure of two quantities was obtained as a function of elevation.

In general, in such control-experiments, it is also desirable to attach a subsidiary contact arm to the moving system, so that a radio signal may be sent out once per cycle in order to inform the receiving station of the exact time of the beginning of any particular part of such a cycle. Failure of the driving-motor would thus also be immediately detected. Five control flights of this type have been carried out successfully, in two of which the instrument was recovered with the driving-motor still running. It is also evident that this type of control is much more satisfactory than the alternative procedure of making two flights, since it would have to be established that the two instruments remained identical at all times during both flights.

ACKNOWLEDGMENTS.

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Wood Tests Aid Airplane Production for Defense. (U. S. Department of Agriculture, Clip Sheet, No. 1208.)—To help aircraft builders meet defense demands, U. S. Department of Agriculture Scientists are seeking better inspection methods for selection of wood now being used increasingly to replace aluminum alloys. For lack of aluminum, manufacturers are substituting wood for metal in training planes and are trying some wood even in fighter craft. Wood is one of the most plentiful raw materials with sufficient strength and lightness for airplanes, but it is subject to decay and other weakening factors. Careful inspection is essential to insure rejection of any wood not of high-quality. Sitka spruce, the wood most valuable for plane construction, is commonly used in wing spars, fuselage and wing ribs, ailerons, stabilizers, and longerons. Propellers for most light planes are of laminated birch or mahogany. Plywood is important for floorboards, reinforcing, and other uses. Research men of the Department of Agriculture say that inspection of wood has improved greatly since the last war. Methods of detecting fungus defects which weaken Sitka spruce were developed toward the close of the World War and are again in use. Now the need is for improvement of methods applied to Sitka spruce and for development of ways to detect rot infections in other woods which may be needed for airplanes as the demand increases. Just published by the Department of Agriculture is Technical Bulletin No. 799, "The Effect of Certain Heart Rot Fungi on the Specific Gravity and Strength of Sitka Spruce and Douglas Fir." It reports research by the Forest Service and the Bureau of Plant Industry on strength of wood infected in varying degrees by heart rot. It is of interest mainly to wood inspectors, airplane plant engineers, and lumber-mill operators handling airplane timber. Improved inspection methods will not only insure high-quality timber for airplane construction, but will enable manufacturers to utilize all suitable wood. Desirable timber is sometimes rejected by factories because of stains thought to indicate rot, when actually the wood is sound. The supply of Sitka spruce is limited and economical use of the timber is necessary. If supplies of spruce run short, it may become necessary for forest pathologists to develop similar methods for inspecting other woods that have possibilities for use in airplanes.

W. P.

A COROLLARY TO THE RING HYPOTHESES.

BY

RONALD L. IVES.

ABSTRACT.

Permian circumpolar glaciations, suggested by some scattered evidence, may be explained as a result of temporarily increased atmospheric opacity, caused by the suspension, in the air, of some of the finer debris resulting from the disintegration of the terrestrial ring system postulated to explain the Permian circumequatorial glaciations. A possible alternation of circumequatorial and circumpolar glaciations is suggested by this approach.

INTRODUCTION.

In a recently published paper,[1] the puzzling circumequatorial glaciations of the Permiam were attributed to the shading effect of a ring system, composed of minute satellites occupying orbits just outside the atmosphere in approximately the plane of the equator. The postulated source of the ring's material was a hypothetical satellite, *Ephemeron*, which came within the Roche Limit just prior to the first Permian ice age and was torn apart by tidal forces.

Climatic fluctuations during this time are attributed to the gradual thinning of the ring system by collisional and other attrition, followed by its rejuvenation as larger fragments of the source satellite disintegrated and supplied the system with numerous new components.

Not explained by this hypothesis in its original presentation were the northward-moving ice sheets of Australia and the Falkland Islands,[2] and the reported Permian glacial deposits of Alaska.[3] This and other evidence, although neither complete nor entirely conclusive, suggests that there were circumpolar glaciations during the Permian, as well as circumequatorial ice sheets.

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[1] Ives, R. L., "An Astronomical Hypothesis to Explain Permian Glaciation," JOUR. FRANKLIN INST., **230**, 45–74, 1940.

[2] Coleman, A. P., "Ice Ages, Recent and Ancient," New York, 144, 149, 1929.

[3] Cairnes, D. D., "The Yukon-Alaska International Boundary, Between Porcupine and Yukon Rivers," Can. Dept. Mines, Memoir 49, 91–93, 1914.

EVALUATION OF EVIDENCE.

If all areas glaciated during the Permian are plotted on a map, and the glaciations assumed contemporaneous, a reasonable extrapolation will suggest that the entire earth was ice-covered during that time; a conclusion contrary to the best and most rigorously checked field evidence. That the Permian ice sheets did not cover the entire earth at one time is shown by the presence of extensive terminal moraines and outwash deposits on several continents, and is as plainly indicated by the continued existence, through the Permian, of many life forms that could not survive a long-continued terrestrial refrigeration.

These considerations lead to the conclusion that the circumequatorial and circumpolar glaciations of the Permian could not have been simultaneous.

CLIMATIC ALTERNATIONS.

During the Permian, climate in the equatorial regions of the earth alternated several times from glacial to nonglacial, as is clearly shown by much field evidence.[4] These alternations, according to the Ring Hypothesis, are the result of changes in the density of the ring; glacial climates occurring when the density was great, nonglacial intervals corresponding to periods of small density.

Into this known climatic sequence must be fitted, in such a way that life was at all times possible on all continents, with the possible exception of Antarctica, one or more periods of world-wide lowering of temperatures of magnitude sufficient to produce circumpolar glaciation. So far as existing evidence goes, these intervals of terrestrial cooling had temperatures not much lower than the present, which is cooler than the average for most geologic time.

To fit these various requisites, it must be assumed that the Permian circumpolar glaciations took place when the equatorial regions were relatively warm. The allowable time for such occurrences, to be in accord with the Ring Hypothesis, must coincide with periods of minimum density of the ring system, and correspond to either circumequatorial interglacial intervals, or those parts of the Permian before the creation, or after the disintegration, of the ring system.

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[4] Coleman, *Op. cit.*, 99, 102, 124, 129, 130, 141, 148, 164, 185.

During parts of these somewhat restricted intervals, conditions resembled, in a minor degree, those of the Pleistocene glacial periods, and the circumpolar glaciations of the Permian may be explained by a simple and reasonable modification of one of the theories advanced to account for the most recent sequence of terrestrial refrigerations.

THE "INVERSE HOTHOUSE" THEORY.

Humphreys[5] attributes the general terrestrial cooling of a normal ice age to the effect of fine volcanic dust suspended in the atmosphere. This dust, within a definite and reasonable size range, blocks off solar radiation, which is of relatively short wavelength, while permitting terrestrial radiation, of relatively long wavelength, to escape into space. The net effect of this atmospheric dust veil is to lower the equilibrium temperature of the earth. This explanation, commonly known as the "Inverse Hothouse Theory," is supported not only by rather rigorous physical calculations, but by large amounts of carefully-collected observational data.

COMBINED HYPOTHESES.

By combining Humphreys' "Inverse Hothouse Theory," as modified to account for the effect of meteoric, rather than volcanic, dust with the Ring Hypothesis advanced to explain the Permian circumequatorial glaciation, an interesting explanation of the Permian circumpolar glaciations, in general accord with both theory and field data, is obtained.

This new hypothesis assumes the substantial correctness of both the Ring Hypothesis and the Inverse Hothouse Theory; attributes the circumequatorial glaciations of the Permian to the shading effects of the hypothetical ring system, and the circumpolar glaciations to a lowering of the equilibrium temperature of the earth by an atmospheric dust veil, produced by the disintegration of the ring system.

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[5] Humphreys, W. J., "Physics of the Air," Philadelphia, 569–603, 1920.

PHYSICAL CONSIDERATIONS.

General Statement.

Physical calculations by Humphreys[6] indicate that only particles having diameters of the order of 1.85 microns are of any great importance in producing the "inverse hothouse effect." Those of much larger dimensions not only reflect terrestrial radiation to a greater degree, so that the inverse hothouse effect is less or even zero, but have a more rapid infall rate, making the continued existence of a dust veil of large particles improbable. Particles having diameters much smaller than 1.85 microns are much less effective reflectors of solar radiation, and as the average range of particle diameters falls far below the critical value (1.85 microns), the inverse hothouse effect again diminishes. Other calculations by the same author[7] indicate that the continued presence of only .001 cubic miles of material, disseminated through the upper atmosphere in the form of dust particles approximating 1.85 microns in diameter, is more than sufficient to cause a general terrestrial refrigeration more severe than any known from the geological record.

Celestial Milling.

Any ring system, whether Saturnian or that postulated about Earth during parts of the Permian, may be likened to a celestial ball-mill, in which the components, by mutual impacts, tend to be shattered into increasingly smaller fragments.

Disrupting forces within this celestial mill are numerous. On very large components, tidal forces are the prime disruptors, but as the average diameters of the members of the system become measurable in feet, rather than in miles, tidal effects become negligible.

In the medium size range, thermal exfoliation and impacts are the most important producers of small fragments. Because most meteors are composed of crystalline rocks, the major products of disruption by thermal changes and impacts will be individual crystals or large fractions thereof, with diameters of the order of millimeters. A few of the fragments produced by impacts of the larger particles will be in the form of fine dust, having diameters measurable in microns.

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[6] Humphreys, W. J., *Op. cit.*, 576.

[7] Humphreys, W. J., *Op. cit.*, 583.

In the small size range, where diameters are less than about one millimeter, particles will be substantially immune to further fragmentation because of their small mass.

Infall Mechanics.

Within the normal collisional atmosphere of the earth, observations reported by Humphreys [8] show that a particle having a diameter of about 1.85 microns takes three years to fall to earth from a height not exceeding 80 kilometers.

Fine dust produced by internal milling in a ring system would require a very considerably longer time to reach the earth's surface, for it must first escape from the ring system by loss of orbital velocity, then penetrate the outward molecular barrage of the krenal [9] atmosphere, and finally fall several hundred miles through the collisional atmosphere.

Should some of these infalling particles carry electrical charges of the same sign as that of the primary, electrostatic repulsion might well delay the clearing of the extreme upper atmosphere for centuries. The effects of such electrostatic repulsion would bear an inverse relation to the size of the charged particles.

The trajectory of a small particle falling to earth from its former orbit in the ring system would be neither a straight line nor any simple curve, but, because of impacts with other particles and with atmospheric molecules, would be the erratic path characteristic of Brownian movements.

Composition of Dust.

Composition of the particles atmospherically suspended to form this hypothetical dust veil is governed primarily by the composition of the ring system from which they are derived. Actually, certain substances, notably malleable metals, would form a smaller proportion of the material of the dust veil than they did of the ring, for such materials cannot be fractured into bodies of the requisite smallness by impacts of ordinary types.

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[8] Humphreys, W. J., *Op. cit.*, 576.

[9] Chamberlin, T. C., "Origin of the Earth," Chicago, 20, 1916.

Consideration of the average composition of planetary material indicates that this dust veil would be composed predominately of silicate particles, it being assumed that Ephemeron, original source not only of the dust, but of the ring system, was not radically unlike known members of the solar system.

Possible Preliminary Ring.

As Ephemeron, parent of the hypothetical terrestrial ring system and source of its material, approached the Roche Limit prior to the first Permian circumequatorial glaciation, it lost, as a result of tidal stresses, its surface layer of thermally-exfoliated debris, heretofore retained by the feeble gravitation of the small satellite. This "skinning" could have occurred many thousands of years before the disruption of the core of the inward spiralling minor moon. The removed material, in accord with planetary theory, formed a ring about the earth, in the approximate plane of Ephemeron's orbit. This preliminary ring, according to necessarily rough calculations, could not have been very dense, and therefore need not have left a very definite climatic record. Collapse of this ring, however, could very well have created an atmospheric dust veil, leading to an early Permian circumpolar glaciation.

Recapitulation.

Physical factors briefly considered in the foregoing sections show plainly that a very small amount of dust disseminated through the upper atmosphere is adequate, provided the particles are of the proper size, to produce notable climatic changes, such as circumpolar glaciations, on earth.

Qualitative consideration of the effects of impacts between members of a ring system composed of normal meteoric materials suggests that a small part of this material could be milled into sizes small enough to produce an effective dust veil in the upper atmosphere of the earth, which would lead to a lowering of the equilibrium temperature of the planet.

Infall of these small particles would be very slow in any instance, and might be inhibited by electrostatic effects, and made erratic by Brownian movements during infall.

Composition of the dust veil is limited by the composition of the terrestrial ring from which it was derived, but the proportion of silicates would tend to be greater in the veil than in the ring.

Consideration of the mode of destruction of the source satellite suggests the existence of a dust veil prior to the formation of the first *dense* ring system, and hence that for N circumequatorial glaciations, $N + 1$ circumpolar ice ages are theoretically possibe.

Conclusion.

According to the reasoning outlined above, the circumequatorial glaciations of the Permian are the result of astronomical effects fully described in the original presentation of the Ring Hypothesis. The circumpolar glaciations of the Permian are attributed to the climatic effects of suspended dust in the atmosphere, a product of the disintegration of the ring system. These circumpolar glaciations are postulated on the basis of field evidence from Australia[2] and the Falkland Islands; that both hemispheres were ice capped is assumed on the basis of evidence from Alaska[3] and a large amount of admittedly disputable and indefinite data from Europe.[10]

If the correctness of the above reasoning is assumed, discovery of evidence of the following Permian occurrences, not reported in available literature, should not be surprising:

1. One or more circumpolar glaciations of Antarctica.
2. Additional glaciation in the northern parts of North America, Europe, and Asia. This ice should be southward-moving.
3. Northward-moving ice in southern South America, and possibly in South Africa.
4. Alternate glaciation of parts of Australia from the polar regions and from the equatorial regions. Evidence that a part of the very extensive glaciation of Australia was of circumpolar origin has been reported.[11]

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[10] Coleman, A. P., *Op. cit.*, 92–96.

[11] Coleman, A. P., *Op. cit.*, 149–150, 152.

Electrical Properties of Neoprene Compositions.—Electrical properties of neoprene compositions, covering the entire range from compounds with high resistivity to those which are electrically conducting, were discussed in a paper presented before the Division of Rubber Chemistry, American Chemical Society, by DR. F. L. YERZLEY. Although neoprene is classed as an insulating material, compounds made from this synthetic rubber have been generally deficient in electrical resistance when compared with a good compound made from natural rubber. This has limited the application of neoprene in the electrical field to those products where high electrical resistivity was not the first requirement, and to oil-resisting protective sheaths over rubber insulation on wire and cable. Dr. Yerzley outlined improvements in neoprene compounding which will increase the electrical resistance of these products and widen their field of application. In the last decade, the d.c. resistivity of neoprene compounds has been raised from 5×10^{11} ohm cm. to 5×10^{13} ohm cm.—a 100-fold increase. The electrical properties of these newer compounds were also compared with those for a range of familiar materials so that the relative position of neoprene with respect to other materials used in the electrical industry could be better understood. Dr. Yerzley also discussed means of rendering neoprene compounds electrically conducting. In many industries and in hospitals the insulating properties of rubber and synthetic rubbers have been a definite handicap. The use of such non-conducting materials on machinery, and on personal equipment, would effectively prevent grounding of the machinery or the person wearing the product. Thus static charges might be built up which would discharge through the air, creating a dangerous condition whenever explosive gases were present. By the use of recently-introduced compounding ingredients, Dr. Yerzley said, it is now possible to produce neoprene compounds as well as rubber compounds which will conduct the static charge from the machine or the person wearing the article to the ground, preventing static build-up and materially reducing the possibility of an explosion from this source. These new electrically-conducting neoprene compounds have the same heat, oil and chemical resistance as do the compounds which have been in use for many years.

W. P.

USE OF THE ACTION FUNCTION TO OBTAIN THE GENERAL DIFFERENTIAL EQUATIONS OF SPACE CHARGE FLOW IN MORE THAN ONE DIMENSION.

BY

KARL SPANGENBERG, Ph.D.

In the study of the behavior of electron tubes the analysis of space charge flow plays an important role. Since the early studies of Child and Langmuir extensive publications on space charge effects have appeared so that the analysis of the subject seems quite complete. Actually this is not so because all analyses to date have been concerned with the one dimensional case. No indication has been given of the attack on a two or three dimensional problem. This is quite a serious omission because with the exception of the simple diode all studies of electron tubes involve two or three dimensions. It is the purpose of this paper to indicate the method of formulation of the necessary equations in the general case of more than one dimension.

In the one dimensional case, that is, in the case of a plane or axial symmetry, solutions of the space charge problem may be obtained directly from Poisson's equation. It is necessary however to express current density in terms of space charge density, and electron velocity in terms of potential. In the two or more dimensional case these relations do not suffice because the electrons do not necessarily move at right angles to the equipotential surfaces. It is therefore necessary to extend the relations involved so that current density may be expressed in vector form.

It is possible to do this by introducing the action function. From the Hamiltonian principle of Least Action it is known that an unrestrained particle will move in a path which is everywhere at right angles to constant action surfaces. In the two dimensional case the electron paths and the lines of constant action form orthogonal sets of curves.

The action function is most readily introduced by using the Hamilton-Jacobi differential equation. The form of this equation to be used here will be that which results when the potential is not a function of time and the particles are presumed to have started from rest at a point of zero potential. With this equation and the three relations used in the one dimensional case there are four equations available. They involve, however, five quantities: potential, space charge density, current density, electron velocity, and action. It is necessary therefore to have one more equation relating the above quantities to complete the set. Such an equation is found in the equation of continuity of current. The resulting set of five equations as written for the two dimensional case then becomes:

Poisson's Equation

$$\frac{\partial^2 E}{\partial x^2} + \frac{\partial^2 E}{\partial y^2} = -4\pi\rho. \tag{1}$$

Total Electron Energy

$$\tfrac{1}{2}m(v_x^2 + v_y^2) - Ee = 0. \tag{2}$$

Vector Current Density

$$\begin{aligned} J_x &= \rho v_x, \\ J_y &= \rho v_y. \end{aligned} \tag{3}$$

Continuity of Flow

$$\frac{\partial J_x}{\partial x} + \frac{\partial J_y}{\partial y} = 0. \tag{4}$$

Hamilton-Jacobi's Equation

$$\left(\frac{\partial A}{\partial x}\right)^2 + \left(\frac{\partial A}{\partial y}\right)^2 = 2emE. \tag{5}$$

In the above equations the symbols have the following significance:

E denotes Electrostatic Potential.
ρ denotes Electric Charge Density.
m denotes Mass of the Electron.
$-e$ denotes Charge of the Electron.
v denotes Electron Velocity.
J denotes Current Density.
A denotes Action $= \int mv\,ds$.

If for compactness the Gibb's Vector notation is used the above equations simplify to

$$\nabla^2 E = -4\pi\rho, \tag{1a}$$

$$\tfrac{1}{2}mv^2 - eE = 0, \tag{2a}$$

$$J = \rho v, \tag{3a}$$

$$\nabla \cdot J = 0, \tag{4a}$$

$$(\overline{\nabla A^2}) = 2emE, \tag{5a}$$

in which the underscored quantities are vectors. If further the constants are omitted so that the resulting equations are simply dimensional, there results

$$\nabla^2 E \doteq \rho, \tag{1b}$$

$$v^2 - E \doteq 0, \tag{2b}$$

$$J \doteq \rho v, \tag{3b}$$

$$\nabla \cdot J \doteq 0, \tag{4b}$$

$$(\overline{\nabla A^2}) \doteq E. \tag{5b}$$

By a simple manipulation of these equations all of the quantities involved can be expressed in terms of the action function. Thus

$$E \doteq (\overline{\nabla A^2}), \tag{6}$$

$$v \doteq \underline{\nabla} A, \tag{7}$$

$$\rho \doteq \nabla^2(\overline{\nabla A^2}), \tag{8}$$

$$J = \nabla A \nabla^2(\overline{\nabla A^2}). \tag{9}$$

These enable one to express everything in terms of the action function. Hence if the differential equation of the action function can be written and its solution obtained, the other quantities can readily be determined. The differential equation can be written without difficulty but its exact solution is not readily obtained in all cases.

From (4*a*), (8), and (9) there results

$$\nabla \cdot \{\nabla A \nabla^2(\overline{\nabla A^2})\} = 0. \tag{10}$$

Although equation (10) seems quite compact when expressed in vector form it is not when the partial differential equation notation is used. For the one dimensional case (10) becomes

$$4\frac{dA}{dx}\frac{d^2A}{dx^2}\frac{d^3A}{dx^3} + \left(\frac{d^2A}{dx^2}\right)^3 + \left(\frac{dA}{dx}\right)^2\frac{d^4A}{dx^4} = 0. \qquad (10a)$$

For the two dimensional case with rectangular coördinates it becomes

$$\begin{aligned} 4A_xA_{2x}A_{3x} &+ 4A_yA_{2y}A_{3y} + A_{2x}{}^3 + A_{2y}{}^3 + 3A_{2x}A_{2xy}A_y \\ &+ 3A_{2y}A_{x2y}A_x + 2A_{2x}A_{xy}{}^2 + 2A_{2y}A_{xy}{}^2 \\ &+ 2A_xA_{2x}A_{2xy} + 2A_yA_{2y}A_{x2y} + A_{2x}A_yA_{3y} \\ &+ A_{2y}A_xA_{3x} + A_{2x}A_{2y}{}^2 + A_{2y}A_{2x}{}^2 \\ &+ A_x{}^2A_{4x} + A_y{}^2A_{4y} + 2A_xA_yA_{3xy} \\ &+ 2A_xA_yA_{x3y} + 3A_xA_{xy}A_{2xy} + 3A_yA_{xy}A_{x2y} \\ &\qquad + A_x{}^2A_{2x2y} + A_y{}^2A_{2x2y} = 0. \qquad (10b) \end{aligned}$$

In (10*b*) the notation A_{x3y} indicates a fourth order partial derivative of A taken once with respect to x and three times with respect to y. It is seen that this equation is quite involved. Like the one dimensional equation it is non-homogeneous and non-linear. It is however symmetrical with respect to the coördinates x and y. It is hoped that equation (10*b*) will come to the attention of competent mathematicians who may be able to surmount some of the difficulties that have delayed the author's solution.

The correctness of the differential equations of the action function is readily shown by an examination of the solution for the one dimensional case. The solution of (10*a*) gives Child's law for the one dimensional case exactly and directly. It also brings to light some trivial physical solutions. This solution will now be undertaken.

Equation (10*a*) is most readily solved by an heuristic method. If we take A to be of the assumed form kx^n and substitute this value in (10*a*) and perform the indicated differentiations there results

$$n^3(n-1)(2n-3)(3n-5)x^{3n-6} = 0. \qquad (11)$$

This identity can only be true if one of the four values of 0, 1, 3/2, or 5/3 holds for n.

Making use of (6) to (9) there results for $n = 0$

$$A = k, \tag{12}$$

$$E = 0, \tag{13}$$

$$v = 0, \tag{14}$$

$$\rho = 0, \tag{15}$$

$$J = 0. \tag{16}$$

for $n = 1$

$$A = kx, \tag{17}$$

$$E = k_1, \tag{18}$$

$$v = k_2, \tag{19}$$

$$\rho = 0, \tag{20}$$

$$J = 0. \tag{21}$$

for $n = 3/2$

$$A = kx^{3/2}, \tag{22}$$

$$E = k_1x, \tag{23}$$

$$v = k_2x^{1/2}, \tag{24}$$

$$\rho = 0, \tag{25}$$

$$J = 0. \tag{26}$$

for $n = 5/3$

$$A = kx^{5/3}, \tag{27}$$

$$E = k_1x^{4/3}, \tag{28}$$

$$v = k_2x^{2/3}, \tag{29}$$

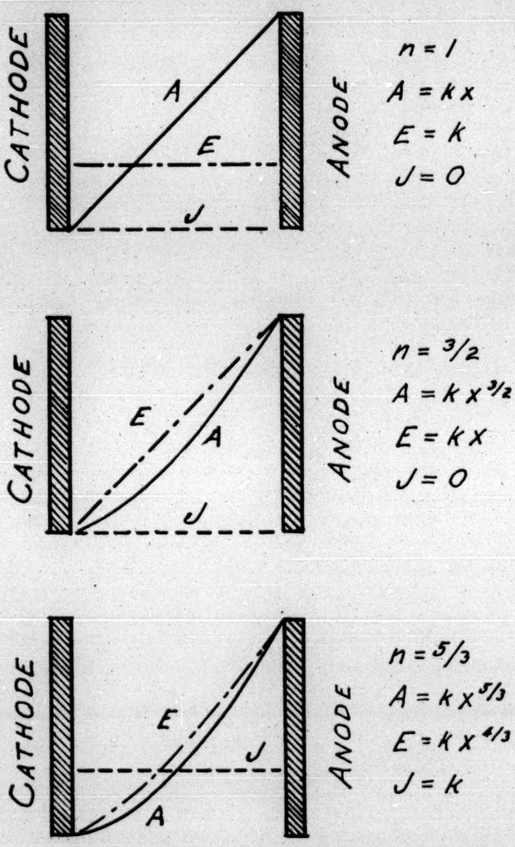
$$\rho = k_3x^{-2/3}, \tag{30}$$

$$J = k_4. \tag{31}$$

Some of the relations for the last three cases are indicated graphically in Fig. 1. The constants above are merely used to express proportionality and do not necessarily have the same value in each case.

It is seen that the case of $n = 0$ is an utterly trivial one.

In the case of $n = 1$ the equations resulting represent the physical case of a cathode and an anode at the same


CATHODE
A
E
J
ANODE
n = 1
A = kx
E = k
J = 0
CATHODE
E
A
J
ANODE
n = 3/2
A = kx^{3/2}
E = kx
J = 0
CATHODE
E
J
A
ANODE
n = 5/3
A = kx^{5/3}
E = kx^{4/3}
J = k

Action, currents, and potential functions of a parallel plate diode.

potential with the possibility of a single electron moving from one to the other with a constant velocity. This is the case that exists when two parallel non-emitting plates are at the same potential.

For $n = 3/2$ the equations resulting represent the physical case of a cathode and anode with an applied potential difference. Here again the equations admit of a single electron being accelerated from plate to the other without disturbing the potential distribution. This case exists when two non-emitting plates have a potential difference between them. Neither this nor the preceding cases have enlightened us much as to what happens in a vacuum diode.

For $n = 5/3$, however, the equations resulting are seen to describe the phenomena which exist when there is an applied potential difference between an anode and an emitting cathode and the current flow is space charge limited. In fact the elimination of the constants between (28) and (31) gives exactly

$$J = \frac{1}{9\pi}\sqrt{\frac{2e}{m}}\frac{E^{3/2}}{x^2}, \tag{32}$$

which is Child's law for parallel plane electrodes.

The above check on the system of differential equations used is quite conclusive. It should be pointed out that solutions of other cases of one dimensional space charge flow are also derivable from the general differential equations. The results of recent analyses of the space charge flow in the grid-anode region of tubes are also readily obtained in this way. It must be recognised, however, that since the differential equation is non-linear, a sum of any two solutions is not a solution. All solutions must be individually derivable from the original equation.

To obtain solutions for two-dimensional problems it is therefore only necessary to obtain the solution of (10*b*). This can perhaps be done by assuming that the solution is a product of a function of x alone and a function of y alone, substituting in the differential equation, effecting a separation of variables, and solving the separate equations resulting. A solution obtained in this way is capable of expressing exactly the complete characteristics of the space charge flow.

Colalloy Armorplate. (*Machinery*, Vol. 58, No. 1504.)—The outstanding characteristic of this armor plate is that it weighs about 50 per cent. less than steel, and is thus particularly applicable to airplane construction. The surface of the new armor plate is claimed to have a hardness much greater than that of ordinary armour plate. It is available in any thickness up to 3 inches, with the hard surface extending to any depth from 0.001-inch to $\frac{1}{4}$-inch. One of the major factors influencing projectile penetration is the heat generated by friction when the projectile passes through the armour plate. Colalloy Armorplate is claimed to have a rate of heat dispersion which is several times greater than that of steel armour plate, thus tending materially to lessen the penetration of projectiles. Another advantage of this material is its hard, highly-polished surface, which does not deteriorate, due to resistance to corrosion and oxidation. This glassy smoothness tends to make a bullet glance or slide off, thus preventing it from "biting" into the metal. The new armor plate is also claimed to have a marked resistance to ice formation. In using Colalloy Armorplate, production bottlenecks can be avoided, it is stated, since each aircraft factory can have its own processing plant, and heat-treating operations or expensive equipment are unnecessary. This material is intended for use in the construction of propellers, wings, fuselages, exposed engine parts, pontoons, struts, tanks, landing gear, and for other vital parts requiring armored protection. It can be supplied in many forms, such as sheets, plates, tubes, angles, and rods, to suit individual production requirements.

W. P.

NOTES FROM THE NATIONAL BUREAU OF STANDARDS.*

THE AURORA OF SEPTEMBER 18, 1941.

The aurora visible over the entire sky at Washington on the evening of September 18 was of great interest in connection with the Bureau's studies of radio wave propagation. Auroras are caused by the electrical excitation of atoms in the rare part of the atmosphere known as the ionosphere. The ionosphere is that portion of the atmosphere from about 30 to 300 miles above the ground which reflects radio waves and makes long-distance radio possible.

Aurora and the accompanying radio, magnetic, and electric disturbances are manifestations of a turbulent condition in the ionosphere. This turbulence is caused by the arrival in the outer atmosphere of charged electric particles. These particles come from the sun, and are usually most prevalent when there are large active sunspots (i.e., sunspots in which visible changes are occurring, new spots being born, etc.). A group of large active sunspots appeared at the edge of the sun September 10. As the sun has one revolution in about 27 days the sunspot group was about at the center of the sun September 17. Tremendous quantities of electric particles were pouring forth from the sun at that time. In northeastern United States aurora was observed nightly starting September 15, and radio reception from European stations was weak, accompanied by a rushing or roaring electric noise on the high radio frequencies. At 1 A.M. E.S.T. on September 18 there was a sudden tremendous increase in the number of electric particles entering the earth's atmosphere from the sun. As a result, the ionosphere was violently agitated, the aurora became visible at Washington, and sky-wave radio transmission was severely disturbed. As the day went on the disturbances increased, culminating in an extremely brilliant auroral display in the evening, and a complete disruption of the ionosphere and of radio transmission.

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* Communicated by the Director.

The auroral display was probably the most brilliant ever observed at Washington. Just after sunset a steady curtain of light appeared in an arc low in the northern sky. Then long bright shafts began to appear and disappear, and the display began to move southward toward the zenith. Shortly before 8 P.M. rays and streamers were visible over most of the sky. Flickering waves of green light appeared to travel upward toward the zenith along the rays. The peak of the display was about 8:15 P.M., and then the aurora began to fade out, most of it disappearing by 11 P.M.

When the aurora was at the peak, the rays seemed to converge to a point near the zenith at about 70° above the southern horizon, and slightly to the east. The reason for this is that the incoming charged particles followed the earth's magnetic field and the rays, which appear along the paths of these particles, are thus everywhere parallel to the earth's field. At Washington, the earth's magnetic field is inclined at 70° to the horizontal and runs from slightly south of east to the northwest. To an observer, then, it seemed as if he stood in the midst of a number of parallel lines of light, whose direction was that of the earth's field. At times of such an aurora it is thus possible to "see" the earth's magnetic field, just as iron filings enable one to "see" the field of a small bar magnet in a laboratory experiment.

A study of the effects accompanying this and other auroras has led to an understanding of what happens. Radio communication is adversely affected, not only during the aurora but for several days afterward. While no aurora was visible at Washington after September 18, high-frequency radio transmission was unusually poor for a week thereafter. Thus the aurora is only an evidence of the first stage of an ionosphere storm, the stage in which there is a tremendous increase in the number of electric particles entering the ionosphere. These particles plunging into the ionosphere tear up the regular ionized layers which normally reflect radio waves, and also produce intense ionization at unusually low levels which uses up the energy of radio waves, thus reducing their intensity in addition to causing severe fluctuations.

During this turbulent stage of the ionosphere storm, high-frequency radio is very erratic, both signals and "static" surge violently, being transmitted with good intensity for short intermittent periods, interspersed with periods of complete failure. This indicates severe turbulence in the ionosphere with small unstable patches or clouds of high ionization densities. Fluttery transmissions can be heard at frequencies far in excess of those normally useful for long-distance communication. Not only auroral but the most severe fluctuations of terrestrial magnetism occur during this first or turbulent stage of the ionosphere storm.

The second stage, following the turbulent stage of an ionosphere storm, is characterized by an expansion and diffusion of the higher ionosphere, extending into latitudes farther south, the greater the intensity of the storm. This expansion and diffusion of the ionosphere increases the virtual heights and lowers the ionization densities of the ionosphere layers. The maximum usable frequencies for night F-layer and daytime F_2-layer transmissions are much reduced because of the lowered critical frequencies and increased virtual heights. Thus the higher frequencies are not usable. Frequencies low enough to be received are usually abnormally absorbed, especially during the daytime. There is usually increased fading and instability of transmissions over night paths. Sky-wave field intensities at broadcast frequencies rise much later at night and reach values much lower than normal.

This second or moderate stage of the ionosphere is what lasts several days. It exists at latitudes as far south as Washington much more frequently than the first or turbulent stage, just as the aurora, which is associated with the first stage, is seldom seen in Washington.

EFFECT OF BRAKE DRUM ROUGHNESS ON WEAR OF BRAKE LININGS.

A research paper (RP1427) in the *Journal of Research* for October gives the results of tests made by Rolla H. Taylor and William L. Holt to determine the relation between the wear of brake linings and the roughness of brake drums.

Five different linings were tested on the Bureau's small inertia testing machine with the following significant results:

1. In general, woven linings seem to be affected more by the roughness of the drums than molded linings. 2. The higher the initial value of roughness of the drum the greater will be the wear. In some cases the wear of a particular lining tested against commercially turned drums was approximately four times as great as when tested against drums which had been given a smooth finish by grinding, or so-called superfinishing. 3. In making wear tests of brake lining, drums of uniform and equal roughness should be used. Furthermore, very smooth drums are greatly to be desired because they give more consistent results and less time is required to obtain reliable data.

These tests indicate that the life of brake lining in service could be increased considerably by the exclusive use of drums having roughness comparable with honed, superfinished, or finely ground drums.

FAILURE OF GAUGE ON OXYGEN TANK.

The recent failure of an oxygen gauge at the Bureau, resulting in injury to a member of its staff, calls attention to a hazard which probably exists in various laboratories.

Gauges used on oxygen tanks are liable to two sorts of explosion: (*a*) simple mechanical breakage under pressure of the Bourdon tube within the gauge, and (*b*) actual explosion due to ignition of oxygen-oil mixtures within the gauge tube. Both types of explosion have occurred at the Bureau. The older gauges, referring to the small gauges 3 inches or less in diameter and on oxygen tanks or oxygen using devices, do not adequately protect the user from the results of breakage or explosion. In general the fronts of the gauges are liable to fly with hazards of glass or other mechanical injury. Newer gauges are so designed as to avoid this danger and most of the gauges purchased in the past few years have this provision.

The hazard of the old gauges still in use appears sufficient to warrant their being discarded and replaced by gauges of the newer, protected design. There are two designs of the latter which have approval of the Underwriters Laboratories. The better of these is known as the "Safety" back design in which the back plate will open in case of excess pressure but is prevented from being thrown off so as to be a source of hazard.

In view of the hazards involved, the Bureau believes that all small gauges (3 inches or less) used on high pressure oxygen should be examined as to their age and design, and replaced by new safety back gauges if they are not provided with this feature. It should be emphasized that *all* gauges used with high pressure oxygen should bear the following warning in a conspicuous place: "*Oxygen—Use no oil.*"

CHANGES IN AQUEOUS EXTRACTS STORED IN GLASS BOTTLES.

Many liquids upon storage in glass containers have been known, at times, to undergo unexpected and undesirable changes in appearance, odor, composition, and alkalinity. Beverages have developed "flakes" high in silica content, which are objectionable from the standpoint of appearance of the product. Neutral saline solutions prepared for intravenous injection have also developed these flakes and have even become toxic because of changes in alkalinity. Serums have undergone alkalinity shifts with accompanying changes in composition, color, and potency; and culture media have shown changes in pH sufficient to render them useless. Since the source of most of these objectionable features has been traced to the quality of glass from which the containers were made, reliable methods for determining the chemical durability of glass are needed.

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In developing such methods for determining the suitability of glass containers for storing liquids, much attention has been given to evaluating the quantity of alkali extracted from the inner surface by distilled water. In a recent investigation by Edgar H. Hamilton and Donald Hubbard of the Bureau's Glass Section, "direct" and "back" titrations of aqueous extracts have been made potentiometrically and with a series of common dye indicators to determine and illustrate what precautions are necessary to obtain reproducible and reliable results. In addition, the results obtained by titration procedures have been compared with conductivity measurements on aqueous extracts from bottles, and these comparisons throw much additional light on the reliability and shortcomings of these two methods.

A paper on this subject (RP1426) will be published in the October *Journal of Research.*

THERMAL EXPANSION OF BORIC OXIDE GLASS AND OF CRYSTALLINE BORIC OXIDE.

James J. Donoghue and Donald Hubbard have been making expansion studies of a boric oxide glass and a sample of crystalline boric oxide using the Fizeau-Pulfrich interference method. The characteristics of the expansion curves for these two materials were found to be very different; the boric oxide glass has a "critical temperature" near 235° C. followed by a very long "neck" with a softening temperature near 320° C., while the crystalline boric oxide has a melting point at 450° to 451° C. This melting temperature for crystalline boric oxide agrees very closely with the value of 450 ± 2° C. reported by F. C. Kracek, G. W. Morey and H. E. Merwin, but differs materially from the value of 294° C. offered by S. S. Cole and N. W. Taylor. The discrepancy between these two values reported for crystalline boric oxide is interpreted in light of the endothermic reaction accompanying the rapid expansion region of fused boric oxide.

The crystalline boric oxide, upon being heated to its melting point, does not return to the crystalline state when cooled, but hardens to a glass. This fact is indicated by comparison of the expansion curves obtained on specimens of the crystalline boric oxide before and after being heated to 451° C.

The detailed report of these measurements will be published as RP1425 in the October number of the *Journal of Research.*

LOCATING THE PRINCIPAL POINT OF AIRPLANE MAPPING CAMERAS.

The demand for increased accuracy in maps from airplane photographs has resulted in steady improvement of the airplane mapping camera. The use of better lenses was soon followed by a desire for specific information on the location of the principal point of the image plane with respect to the collimation index markers mounted on the four sides of the focal plane frame. The principal point of the image plane, defined as that point where a perpendicular dropped from the rear nodal point of the lens intersects the image plane, is not readily located, but a method has been developed by Francis E. Washer of the Bureau's Optical Instruments Section by which this can be accomplished.

The chief factors in the location of the principal point are (1) to locate the image of an infinitely distant object, lying on a perpendicular to the image plane, with respect to the collimation index markers of the camera, and (2) to determine how much the position of this image is altered by prism effect in the lens. A method for measuring these quantities has been devised and tried on a total of 40 or more precision airplane mapping cameras that are to be used on various governmental mapping projects. The method is described and tabulations of results are given for a representative group of cameras in RP1428 in the October number of the Journal of Research.

PRIORITIES IN MATERIALS FOR VEHICULAR LAMP AND SIGNAL EQUIPMENT.

Under the auspices of the Civilian Allocation Division, Office of Production Management, a conference was held in Washington on September 11, on the conservation of strategic materials in the manufacture of lamps and signal equipment for vehicles. The conference listed the following items of equipment under headings to indicate the relative necessity of each group, and including some items which are necessary for a relatively small number of vehicles, weather conditions, or situations: I. Required by law or regulation for all vehicles—Headlamps, tail lamps, license-plate lamps, stop lamps, and rear-view mirrors. II. Required by law or regulation as additional equipment for commercial vehicles—(*a*) Regular items: Clearance lamps, marker lamps, identification lamps, reflex reflectors, and direction signals. (*b*) Emergency equipment: Oil-burning flares, red electric warning lanterns, reflective flares, fire extinguishers, hand axes, first aid kits, fuzees, flags, skid chains (also needed for passenger vehicles), defrosters (also needed for passenger vehicles), tow chains, and tools for ordinary road repairs. III. Safety devices—(*a*) Outside of vehicle, permissible if approved by State or regulatory body: Fog lamps (adverse-weather lamps), supplementary driving and passing lamps, parking lamps, spot lamps, turn indicators, back-up lamps, back-up alarms, and burglar alarms. (*b*) Inside of vehicle: Instrument panel lights, dome lights, and destination lights. IV. Catchpenny items of equipment—Believed unessential to safety: Fender guides, exhaust deflectors, ornamental radiator emblems, ornamental gear-shift balls, license-plate rims and enclosures, and all novelty attachments.

The conference recommended that items falling under the fourth classification be considered as postponable needs and, as far as they involve strategic materials, should not be manufactured during the unlimited emergency. It was the consensus that in order to conserve strategic materials: (*a*) The States should be requested to follow the Uniform Vehicle Code as to kind and number of items required, and (*b*) items manufactured during the emergency should conform to Nationally-recognized standard minimum specifications.

Mr. Smiley stated that materials would be allocated for production of essential items of lamps and signal equipment necessary for the safety of vehicles.

Those attending the conference were: John B. Smiley, Civilian Allocation Division, OPM (chairman); Frank H. Crockard, Civilian Allocation Division, OPM; Robert Beatty, Metal Section, OPM; H. H. Allen, Safety Section, Bureau of Motor Carriers, Interstate Commerce Commission; R. S. Armstrong, Manager, Safety Equipment Manufacturers Assn.; I. J. Fairchild, chief, Division of Trade Standards, National Bureau of Standards; L. S. Harris, executive director, American Association of Motor Vehicle Administrators; J. L. Koubek, Guide Lamp Division, General Motors Corporation (representing Automobile Manufacturers' Assn.); James J. Shanley, chief, Testing Division, Department of Motor Vehicles, Trenton, New Jersey, also Chairman Engr. Com., American Association of Motor Vehicle Administrators.

THE FRANKLIN INSTITUTE.

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The library and reading room are open on Mondays, Tuesdays, Fridays and Saturdays from nine o'clock A.M. until five o'clock P.M., Wednesdays and Thursdays from two until ten o'clock P.M.

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NOTES FROM THE BARTOL RESEARCH FOUNDATION.

AN INVESTIGATION OF THE PROPERTIES OF PROPORTIONAL COUNTERS. I.*

BY

M. E. ROSE AND S. A. KORFF.

A theoretical and experimental investigation of the amplification properties of proportional counters has been made. On the basis of a discharge mechanism in which the amplification is due to electron avalanches the theory has been developed with the following primary assumptions: (1) All secondaries are produced by electron impact with no photon emission in the counter gas and thus no photoelectric emission at the cathode; (2) fluctuations in energy loss and specific ionization are neglected. The analysis involves the determination of the average number of ionizing collisions per unit distance (average energy) as a function of position in the counter, and the spatial extent of the ionization region near the wire anode. The former quantity is calculated explicitly in terms of the constants of the counter and the latter is shown to be simply related to the threshold voltage for proportional amplification, and is most suitably determined from the measurements. The gas fillers used in the measurements of the amplification factor were, for the most part, methane-argon mixtures of various relative concentrations and total pressures. In addition, other polyatomic mixtures, illuminating gas, BF_3-A and ether-A were used. Comparison of theory and experiment gives quite satisfactory agreement in all cases but two: large A concentration (50 per cent. or more at a total pressure of 10 cm. Hg) and low total pressure (5 cm., or less, with a mixture containing 90 per cent. CH_4). In the anomalous cases the measured amplification factor rises extremely rapidly and such mixtures are therefore somewhat

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[*] An abstract of an article published in full in *The Physical Review*, **59**, 850 (1941).

undesirable for stability reasons. This unstable behavior is characteristic of gas mixtures of the monatomic and/or diatomic type. An explanation of the difference in amplification properties of the polyatomic and simpler type gases is proposed. It is shown that while photon emission in the ultraviolet and subsequent contributions to the avalanche by photoelectric emission at the cathode is to be expected for the simpler gases, polyatomic gases should effectively quench such photon emission by virtue of greater energy loss of the slower electrons in exciting molecular vibrations and rotations. Moreover, appreciable emission of ultraviolet light by polyatomic molecules under electron bombardment is not to be expected. This explanation receives confirmation from cathode tests which were performed: measurements of pulse size, or amplification factor, for solid and perforated, oxidized and non-oxidized Cu cathodes. Further support of these arguments is found in experiments of other investigators: energy loss and mean free path measurements, electron bombardment of gases in a photo-cell. Finally, specific recommendations as to desirable pressure and concentration in the CH_4-A mixture are given.

NUCLEAR PARTICLES IN THE COSMIC RADIATION.*

BY

S. A. KORFF.

A series of balloon flights employing proportional counters has been carried out. In these flights the instrument measures the number of events liberating more than an assignable minimum of ionization in the instrument. The contribution due to each of several types of such events is evaluated, the effect of large showers is considered and instrumental errors are discussed. It is found that alpha-particle counts due to slow-neutron-induced boron disintegrations may account for about one-third of the discharges observed with BF_3 counters. Counters in which other gases are used permit an estimate to be made of the flux of highly ionizing particles, mostly protons,

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* An abstract of an article published in full in *The Physical Review*, **59**, 949 (1941).

which is found to be about 10^{-3} per sq. cm. per sec. These data permit the calculation of the rate of production of protons, which is found to be of the same order as that of neutrons, namely about 5×10^{-2} per gram per sec. at the altitude corresponding to 2 meters of water equivalent below the top of the atmosphere. The energy distribution, the amount of the flux and the altitude dependence suggest that both protons and neutrons are produced about equally by a process or processes connected with the soft component of the radiation.

NOTES FROM THE BIOCHEMICAL RESEARCH FOUNDATION.

The Determination of the Distribution of Bacteria in the Rat by the Use of Radioactive Isotopes.—J. O. ELY. Methods of studying the distribution of bacteria after introduction into the animal body have heretofore been confined to microscopic examination or the culture of samples of tissues. A new method has become available with the production of radioactive isotopes of many of the common elements. It is probable that most species of bacteria utilize one or more of the elements which can be made radioactive. If these radioactive elements, in suitable compounds, be introduced into the culture medium the bacteria may incorporate them into the compounds of their bodies. The bacteria are then tagged so that they may be traced. For instance, Williams, Sandholzer, and van Vorhees (*Journal of Bacteriology*, **39**, 19, 1940) have reported the incorporation of radioactive phosphorus in the nucleoproteins and phospholipids of *Escherichia coli*. Franklin (*Science*, **89**, 298, 1939) reported the incorporation of radioactive sulfur into the glutathione molecule by yeast.

Preliminary experiments have been carried out with this radioactive method using *E. coli* and *Staph. aureus*. The bacteria were grown for 18 hours on agar slants of heart infusion broth to which had been added a small amount of radioactive sodium phosphate (phosphorus was the radioactive element) prepared from material irradiated by our cyclotron. The organisms grown under such conditions were found to possess a sufficient amount of the radioactive isotope for tracing after introduction into the rat.

The bacteria were removed from the surface of the medium with distilled water and were washed four times in 400 times their volume of distilled water. They were then suspended in 0.85% sodium chloride for injection into rats.

Albino rats were used. Injection of the bacteria was made intravenously into a vein of the tail. The volume of the inoculum in each case was 1 cc. and contained the equivalent of 0.0027 cc. of packed bacteria (measured by centrifugation in a graduated capillary centrifuge tube). Thirty minutes after the injections the animals were decapitated and various tissues and organs removed. The wet organs were weighed and suitable portions taken for ashing. The tissues were ashed in small procelain crucibles and the radioactivity measured by placing the crucibles beneath the tube of a Geiger-Mueller counter.

Results.

Tissue	*E. coli* Rat No. 1, Male. 148 grams.		*E. coli* Rat No. 2, Male. 150 grams.		*E. coli* Rat No. 3, Male. 168 grams.	
	Relative radio-activity per gram of wet tissue.	% of inoculum in organ or tissue.	Relative radio-activity per gram of wet tissue.	% of inoculum in organ or tissue.	Relative radio-activity per gram of wet tissue.	% of inoculum in organ or tissue.
Kidneys	1.00	1.16(both)	1.00	4.76(both)	1.00	0.95(both)
Testicles	2.03	3.28 “	0.17	1.41 “	0.58	0.95 “
Brain	0	0	0.17	0.70	0.58	0.48
Spleen	5.13	4.88	2.53	6.43	5.76	9.05
Lungs	4.46	11.53	5.87	20.95	6.53	5.02
Liver	8.87	42.04	1.60	49.08	7.58	45.50
Lymph glands	34.2		5.80		26.55	

Tissue	*Staph. aureus* Rat No. 4, Male. 154 grams.		*Staph. aureus* Rat No. 5, Male. 175 grams.	
Kidneys	1.00	1.13(both)	1.00	1.50(both)
Testicles	0.43	1.13 “	0.09	0.25 “
Brain	0.29	0.28	0	0
Spleen	4.33	4.80	1.30	2.38
Lungs	19.33	12.70	7.60	10.00
Liver	11.33	67.20	5.42	44.50
Lymph glands	8.33		6.35	
Thymus			0	0
Muscle (Gastrocnemius)			0	0
Intestines			0.28	
Heart			0.37	0.25
Tibia			0.34	
Blood			0.21	

It may be seen from the data that, under the conditions of these experiments, the liver, as an organ, contained a much greater proportion of the bacteria injected into the blood than did any of the other organs. The lungs were the organs which usually contained the next largest amount. Rat number 3 was an exception in this respect, the spleen containing more than the lungs. In this animal, however, the spleen was approximately twice the size (by weight) of the spleens of the other animals.

The brain, apparently, has an effective means of preventing these bacteria from entering it in large numbers.

While this method of tracing bacteria in the animal body may be very useful, it probably will be found to have certain limitations which will need investigation. In long time experiments disintegration of the bacteria, also the normal metabolism of some of the bacteria in the animal tissues and exchange reactions between the radioactive compounds in the bacteria and compounds of the animal body liberating the radioactive element from the bacteria, would vitiate the results. In short time experiments, however, where there is little danger of much disintegration of the bacteria the method should be applicable.

Further investigations of the method are being undertaken.

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BOOK REVIEWS.

PHYSICS FOR SECONDARY SCHOOLS, by O. M. Stewart and B. L. Cushing, 760 pages, illustrations, plates, 14 × 20 cms. Boston, Ginn and Company. Price $1.80.

The manner of presentation of the subject of physics to secondary school students has long been recognized as of extreme importance. Interest must be stimulated and held above all, while an understanding of the principles is inculcated. Various methods and means have been devised for doing this. Some have been discarded and others improved so that the modern text is the result of much trial. Physics is a subject that is becoming increasingly useful in everyday life and is therefore being taught to a greater number of students, regardless of the kind of special education likely to follow the secondary school. This puts an added burden on the text used.

The book at hand is in its revised edition, having been originally published in 1932. It has had extensive use and is therefore well known. Covering the subjects of mechanics and heat, electricity and magnetism, sound and light, electrical emissions and atomic transformations, it is typical as a modern text utilizing ingenious illustrations of specific examples seen "on the street" and these are up-to-date. It must be borne in mind that a period of only nine or ten years brings changes that the younger students have not experienced.

One of the faults of the older texts has been that the topics which make up the subject of physics were taught as distinct from each other. It is satisfying to see the attempt made in this book to correlate the topics and at the same time give proper weight to the other factors to sustain interest and create desire for more knowledge. Often the young mind is prone to grasp certain topics and disregard others. This feature of the book tends toward an evenness of knowledge distribution over all the topics.

The book contains numerous teaching aids. It is flexible and adaptable to courses of different length and intensity. The illustrations, problems, questions and summaries, and many other features make it valuable as a text for the class of student to whom it is directed.

R. H. OPPERMANN.

COLLEGE PHYSICS, by Henry A. Perkins, 568 pages, illustrations, 16 × 23 cms., New York, 1941, Prentice-Hall, Inc. Price $3.50.

The author, in the preface states, "College Physics, of which this is an abridged edition, was written with the purpose of offering such complete explanations of principles and theoretical deductions that the student would understand them without assistance from the instructor." The book at hand is not strictly an abridgment, for there is not much evidence of condensation, and clarity apparently has been preserved. What has probably taken place is that material has been eliminated. The original work, it is easy to see, might have been quite voluminous and probably contained much doubtful material under the classification of fundamental physics. The abridgment contains some 567 pages of text.

The subjects covered are those usually covered in texts on fundamentals—mechanics, heat wave motion and sound, light, electricity and magnetism, and corpuscular physics. The treatment is rigorous and coverage rather complete. The author stays close to the subject matter with little attention being given to practical application of it in the text proper. Examination of the problems for exercise at the end of each chapter reveals the presence of the practical application feature here. A supplemental laboratory course also provides opportunity for this which of course is not within the scope of this book. Necessarily a book on this subject requires considerable space devoted to diagrams, curves and photographs. This book is well supplied with them. An appendix contains general information for the solution of the problems such as tables of physical constants, tables of logarithms and natural trigonometric functions. The subject index in the back adds to the value of the book as a reference.

There are many situations in the teaching of the fundamentals of physics where this book will be valuable as a text. It will also be found valuable as a reference work, and those who wish to use it to "brush up" their knowledge of fundamentals will find here a ready work, modern in subject matter as well as technique of presentation.

R. H. OPPERMANN.

EMULSIONS AND FOAMS, by Berkman and Egloff, 591 pages, illustrations, 15 × 23 cms. Reinhold Publishing Corporation, 1941, New York. Price $8.50.

Here is a subject that will attract the attention of many in a variety of industries, for the difficulties or advantages of emulsions and foams have long been recognized. Necessarily based on many hundred literature and patent references, all of which are noted, the book is designed to provide a theoretical and practical background useful in attacking problems on emulsions and foams.

That there is much to be learned about the subject is early pointed out, for it is stated that a great many investigators have studied the nature of emulsions, their properties, formation, destruction, and stability, but usually only a single system has been studied at a time and that with one or two significant factors or characteristics. No one system has been investigated in its many phases. It is with this that the book begins—a review of these factors and characteristics after which, in summary, a manner in which future investigations should be carried out viz.—(1) a logical and separate grouping of factors influencing emulsification, permanence of system formed, and its transition from one type to another, (2) more accurate methods of investigation, (3) only emulsion systems similar in nature and type should be compared with respect to their various properties, and then only under comparable conditions.

With regard to foams, the origin and mechanism of foam formation, the stability of foam systems, and the transition to the unstable state are treated as the three differentiated stages. Up to this point the theoretical aspects of the subjects are treated.

Practical knowledge of emulsions constitutes the greater portion of the book. This begins with methods of preparing emulsions, the emulsification process and types of equipment used for emulsification. Demulsification is next taken up—the methods used, such as heat treatment, action of chemicals and agents, freezing and diluting, etc. Attention is given asphalt and bitumen emulsions with regard to road construction, and lubrication oil emulsions.

The last part of the book is devoted to a description of laboratory methods used in the examination of emulsions.

The book is the result of an exhaustive search of the literature on the subject coupled with a broad knowledge and the ability of good presentation. A comprehensive subject and author index adds much to the value of the book for reference purposes. The authors need no introduction to followers of this type of literature and they have presented a book that has wide applications.

R. H. OPPERMANN.

THE ART OF RETOUCHING AND IMPROVING NEGATIVES AND PRINTS, by Robert Johnson, 14th edition, revised and enlarged by Arthur Hammond. 158 pages, illustrations, 16 × 24 cms. Boston, American Photographic Publishing Co., 1941. Price $2.50.

The present work is now appearing in the 14th edition, and this long series of editions in the last thirty years should be a good recommendation of its usefulness. The part that retouching plays in photography is important. The lens of the camera sees more than the eye, in fact often sees too much and that is when retouching comes into its own. The work is divided into two parts under ten chapters. It covers materials, tools, methods and much work on portrait negatives.

Part two deals with the finishing and coloring of photographs, monochrome finishing, airbrush, water coloring and finishing in oil colors.

The book contains much information for the photographer and retoucher.

W. A. R. PERTUCH.

FUNDAMENTALS OF PHYSICAL SCIENCE, by Konrad B. Krauskopf, 660 pages, illustrations, 16 × 23 cms. McGraw-Hill Publishing Company, 1941, New York and London. Price $3.50.

Elementary treatises on subjects such as physics often resort to the more spectacular accomplishments in order to make the presentation more easily readable and to stimulate interest. This is particularly true when the work is directed toward those who do not intend to specialize in physics or where only a general knowledge of physics is needed in conjunction with other subjects. The effectiveness of this is of course dependent on many factors. The danger lies in a lessening of emphasis on how these accomplishments were made possible, and the choice of the accomplishments may leave out those having important points. In other words—too much "sugar coating."

The author of this book seeks a solution of this problem by stressing the methods of scientific reasoning rather than their results and he does this by means of clear explanations sprinkled sparingly with some simple mathematics leading up to the illustration of this accomplishment. This is the general plan. A typical example is in electricity where the principles of physics are first laid down, in a not too technical way, leading up to practical machinery like large commercial electromagnets, the motor and the transformer. The stress is on the principles, not the machines. The topics covered include the solar system, matter and energy including an explanation of the language of chemistry, the structure of matter covering electric currents, fundamental processes like ionic reactions, and the biography of the earth.

An examination of the book reveals an ingenious co-mingling of what mathematics may be consumed with the physics unknowingly or that an impression may be created that the mathematics and physics are inseparable. In either case little harm is done, for the manner of presentation is such as to avoid confusion and facilitate understanding.

A more rigorous training is provided when the student reaches the end of each chapter and attempts to answer the questions found there. Proper supplemental classroom instruction will round off the difficulties encountered.

The ideas and materials in the text have been developed in the well-known pioneering course in physical science in Stanford University. For the beginning student the book has many advantages and teachers of elementary prnciples will find its coverage and methods of value. The general reader too will find the subject matter presented in an interesting and informative way.

R. H. OPPERMANN.

INTRODUCTION TO PHYSICAL OPTICS, by John Kellock Robertson, Third Edition, 512 pages, illustrations, plates, 15 × 23 cms., New York, D. Van Nostrand Company, Inc., Price $4.00.

Rapid advances in this field in recent years have placed an unprecedented demand for up-to-date introductory texts. Certainly recent discoveries have laid open a vast field, the significance of which is as yet unknown. Attention is therefore drawn to the subject for an opportunity of exploration as well as the fact that the new discoveries have in themselves broadened the usefulness of optics so that a general knowledge of modern views of light is often indispensable in other branches of science.

This book is in its third edition, the two previous editions having been in 1929 and 1935. The author states that this third edition embodies some of the recommendations of Prof. Rud Nielsen's committee on the Teaching of Geometrical Optics. The text opens with an explanation of why we study wave motion followed by a thorough discussion of it and its light ramifications. Reflection and refraction on Huygens' Principle leads to the discussion on vision through the telescope and microscope, the latter containing material introduced for the first time. Other topics covered are dispersion; the fundamental facts of spectroscopy, the theoretical significance of which are taken up later; a consideration of interference leading to various means of evaluating wave lengths; diffraction showing that light does not travel in straight lines and that by combining a modification of Huygens' Principle with the principle of interference after the manner of Fresnel, approximate rectilinear propagation results for a wave motion in which the wave-lengths are very small in comparison with the dimensions of ordinary obstacles and openings; and polarized light. The electromagnetic theory of light is introduced at this point. The ultimate source or origin from which light waves eminate is next taken up leading to radiation potentials; absorption and band spectra.

Here a brief review is made of the material so far presented and consideration is given to the differences of the wave theory and other optical phenomena, notably those referring to the interaction between radiation and matter which can only be explained in terms of a quantum theory. The last chapter of the book is devoted to the question, "Can the existence of an ether be detected?"

The text is thoroughly technical, a treatment giving little time or space to other than what directly bears on the subject. Problems at the end of chapters give thorough exercise and these are supplemented by additional problems at the end of the book. Answers to all problems are provided.

The book represents a completeness of treatment as far as an introduction should go, which aims to give a desire to go more deeply into the subject.

R. H. OPPERMANN.

THE THEORY AND APPLICATIONS OF HARMONIC INTEGRALS, by W. V. D. Hodge, 281 pages, 14×22 cms. New York, Cambridge University Press, 1941. Price $4.50.

A type of space important in various branches of mathematics is that of the classical Riemannian geometry. It is a flexible space and knowledge of it therefore becomes broadly useful. This book is devoted to the study of certain integrals defined in the space, the theory of which it is possible to employ in any field of mathematical research in which a Riemannian manifold plays a part.

The book originally was a section of an essay for which the Adams prize of 1936 was awarded. It has been revised and rewritten and a chapter added dealing with the application of the harmonic integrals to the theory of continuous groups. The book opens with a treatment on Riemannian manifolds sufficient in extent to lay the groundwork for what follows. Integrals and their periods is next taken up, in which proof is given of de Rham's theorem on the existance of an integral with assigned periods. Following this, a discussion of harmonic integrals contains proof of the fundamental existence theorem for these integrals.

The last two chapters are devoted to applications where use is made of the results obtained heretofore. Investigation is first made of the properties of algebraic varieties. Here it is explained how to construct a set of Riemannian manifolds corresponding to an algebraic variety of complex dimensions and then there is investigated the properties of the harmonic integrals on one of these manifolds. Later, consideration is given to the application of the theory of harmonic integrals to spaces which possess continuous groups of transformations into themselves. It is shown that when a space possesses a continuous group of transformations into itself and the group fulfills certain general conditions, a Riemannian metric can be defined in the space by means of this group, and the harmonic integrals associated with this metric are invariants of the group.

The book is helpful in bringing enlightenment to those who may have need for the application of knowledge of harmonic integrals.

R. H. OPPERMANN.

MATHEMATICAL TABLES, by Herbert Bristol Dwight, 231 pages, 14 × 23 cms. McGraw-Hill Publishing Company, Inc., New York. Price $2.50.

This book contains tables conveniently arranged for ready use. In the trigonometric tables, decimals of degrees, to the 1/100 degree, are used instead of degrees, minutes and seconds which are in many ways less convenient than decimals. The author points out that this is in conformity with the fact that a growing number of mathematical results are now in decimals of degrees and to use these it is almost necessary to employ tables of sines and tangents, etc. of decimals of degrees such as those here given. The tables include the sin, cos, and tan of thousandths of radians as well as $\sin^{-1} x$, $\cos^{-1} x$ and $\tan^{-1} x$.

The exponential functions e^x and e^{-x} are also given. A large part of the book is given over to hyperbolic functions. Binomial coefficients, Gregory-Newton interpolation coefficients, surface zonal harmonics, elliptic integrals, the Riemann Zeta function and other useful tables are also included. The book is valuable to those who do calculating involving such data.

R. H. OPPERMANN.

STRENGTH OF MATERIALS, PART 2, ADVANCED THEORY AND PROBLEMS, by S. Timoshenko, second edition, 510 pages, illustrations, 16 × 23 cms. New York, D. Van Nostrand Company, Inc. Price $4.50.

Almost every student and engineer who has to do with strength of materials in the past ten years is familiar with Timoshenko. The first edition of the work has been very popular in its exposition of new developments and the derivation of problems of practical interest. The second edition, of which this is part two, comprises a change, in the way of bringing the subject matter up-to-date. It is devoted to advanced theory and problems supplementing part one, which was reviewed in these pages sometime ago and which dealt with elementary theory.

The general character of the work has remained unchanged. There are nine chapters viz.—special problems in bending of beams, curved bars, thin plates and shells, buckling of bars and plates and shells, deformations symmetrical about axis, torsion, stress concentration, deformations beyond elastic limit, mechanical properties of materials. New material added has special interest with regard to airplane construction as well as in other directions.

This edition retains its masterful method of presentation. There should be a larger demand for its use due to the additional material that it contains being both theoretical and practical.

R. H. OPPERMANN.

CHEMICAL ENGINEERING CATALOG, 1941–42. Twenty-sixth Annual Edition. 1214 pages, illustrations, 22 × 29 cms. New York, Reinhold Publishing Corporation.

The Committee on the Chemical Engineering Catalog has in this twenty-sixth edition published a vast amount of material to make this work an up-to-date reference book on technical chemistry. The arrangement is practically the same as the former edition. The present volume is enlarged and well indexed in reference to trade names, equipment, chemicals and manufacturers' catalogs. The technical and scientific book section lists many worth while books.

P.

HANDBOOK OF CHEMISTRY, by Norbert A. Lange, Ph.D., a reference volume for all requiring ready access to chemical and physical data used in laboratory work and manufacturing. 1909 pages, 14 × 20 cms. Sandusky, Ohio, Handbook Publishers, Inc., 1941. Price $6.00.

Continued accomplishment in any scientific endeavor more often than not depends upon the obtaining of up-to-date accurate data and information with despatch. The old maxim "time is money" has no better application than in the fields of chemistry and allied sciences, and any means of saving is a welcome contribution. The handbook always has been a useful tool. Of late, however, the lines separating the branches of science have become indistinct so that handbooks, to be effective, must cover more area than their specific titles would imply.

Perhaps the best feature of "Handbook of Chemistry" is the recognition by the authors of this fact. The work is in its fourth edition, the third being only two years old. And much of the new material and rearranged material relates to that which is helpful to chemists, yet is somewhat removed from chemistry per se. For instance, among the new tabular data can be found information on sensitive lines of the elements, tank and pipe capacities, and binomial coefficients. Further, the data here presented reaches into mineralogy, biology, materials of construction, flow of fluids and even the two hundred year calendar. An appendix gives mathematical tables and formulas.

With all this great quantity and variety of data the handbook would be of little value if the specific data needed at any time could not be located quickly. The index provides the answer to this question. It is exhaustive, complex, yet comprehensive. The number of cross indexes of the subjects is certainly sufficient for any use as can be seen by testing it.

The handbook is an essential fact finding tool. The material contained in it is authoritative and arranged in an orderly manner. Directed for the use of the chemist, it has much of value for workers in many other fields and therefore should be within reach of all.

R. H. OPPERMANN.

COLLEGE PHYSICS, by John A. Eldridge. Second edition, 702 pages, illustrations, 15 × 22 cms. New York, John Wiley & Sons, Inc., 1940. Price $3.75.

The author of this book, in the preface, states very definitely the purposes that he had in mind for it. "I have tried to write a textbook which will appeal to the student with only a general interest in the subject—non-science majors—and a textbook which will at the same time give a solid foundation for the student with a direct professional interest in physics. Also, a textbook which will be suitable for a student with no previous training in the subject, yet in point of view and selection of material will impress the student with High-School physics, as in no sense a mere redoing of his earlier work. And a book in which the student will think through the subject for himself."

To the student or prospective student this statement has much appeal. He cannot go wrong. To the more mature scholar or teacher of physics, it has a broader and more definite meaning, the fulfillment of which is the goal of every teacher. As might be expected the principal feature is the language and method of presentation. Extreme effort is made to make it easily readable and considerable space is devoted to this end. The trend proceeds from a discussion of the relationship between physics and civilization into the constitution of matter, effects of heat, the characteristics of sound, electricity, magnetism, thermionic emission, and light. This order of subjects is somewhat different than other presentations, but it is bound up in a unified whole.

In accordance with the expressed purpose of the author, the mathematics required coincide with the simpleness of treatment. By the diligent use of the questions and problems at the end of chapters it is entirely possible to obtain from the book a course of home study with little or no classroom instruction. The book is profusely illustrated and in the way of making it self-contained the author includes appendixes reviewing the mathematics of proportion, and giving help in developing the correct habits in the solution of problems.

The text is flexible in-so-far as sections are marked which may be omitted without affecting the continuity of the course, should it be desired to eliminate parts of less general interest. Great effort has been taken to accomplish the stated purpose of the text and it is certainly a valuable work for those who fall in the category of needing it.

R. H. OPPERMANN.

PUBLICATIONS RECEIVED.

The Calculus of Extension, by Henry George Forder, 490 pages, 14½ × 22½ cms., The Macmillan Company, New York. Price $6.75.

The Second Yearbook of Research and Statistical Methodology, Books and Reviews, edited by Oscar Krisen Buros, 344 pages, 20 × 28 cms., The Gryphon Press, New Jersey. Price $5.00.

Surge Phenomena, Seven Years' Research for the Central Electricity Board (1933–1940), edited by The British Electrical and Allied Industries Research Association, 426 pages, illustrations, 23 × 29 cms., London, The British Electrical and Allied Industries Research Association. Price £2. 10 s.

Photoelasticity, by Max M. Frocht, 401 pages, illustrations, plates, 16 × 24 cms. New York, John Wiley & Sons, Inc. Price $6.00.

Elements of Electrical Engineering, by Arthur L. Cook, 611 pages, illustrations, 16 × 24 cms. New York, John Wiley & Sons, Inc. Price $4.00.

Benjamin Franklin's Experiments, by I. Bernard Cohen, 435 pages, 15 × 22 cms. Cambridge, Mass., Harvard University Press. Price $4.00.

Electrical-Engineering Fundamentals, by George F. Corcoran and Edwin B. Kurtz, 450 pages, illustrations, 16 × 24 cms. New York, John Wiley & Sons, Inc. Price $4.00.

An Introduction to Physical Statistics, by Robert Bruce Lindsay, 300 pages, illustrations, 16 × 24 cms., New York, John Wiley & Sons, Inc. 1941. Price, $3.75.

A Textbook in Electricity and Magnetism, by Harry C. Kelly, 346 pages, illustrations, 16 × 24 cms., New York, John Wiley & Sons, Inc. 1941. Price, $3.75.

Practical Solution of Torsional Vibration Problems, by W. Ker Wilson, Volume II, Second edition, 694 pages, illustrations, 15 × 22 cms., New York, John Wiley & Sons, Inc., 1941. Price $8.50.

Galois Lectures, by Jesse Douglas, Philip Franklin, Cassius Jackson Keyser, Leopold Infeld, 124 pages, 13 × 19 cms., New York, Scripta Mathematica, Yeshiva College. Price $1.25.

CURRENT TOPICS.

Largest Shell-Loading Plant Goes Into Operation.—(Chemical & Metallurgical Engineering, Vol. 48, Number 8.) The Iowa Ordnance Plant at Burlington, Iowa is one of the largest shell-loading plants in the world. It will cost $30,000,000 and will require 7,000 employees. The plant will load artillery shells, bombs, and the corresponding components. Each loading line was scheduled for completion August 1, while the bomb-loading line and the detonator line are scheduled for completion soon thereafter. The loading buildings are divided into many small rooms separated by protective walls of reinforced concrete. The roofs and outer walls are of light, corrugated asbestos which would reduce the force of explosions. All electric light fixtures in the plant are of special design for rapid diffusion of heat. Floors of all rooms where men work with explosives are of specially finished, smooth, waxed concrete that cannot collect dust particles. Empty shells are received in a building as clean and bright as a new dairy. So much of the loading process is automatic that, from the time the shells arrive until they are taken from the end of the line, they are seldom touched by a human hand. Shell loading is done on a production line roughly similar to an automobile assembly line. Revolving machines carry the empty shells through paint spray booths. After painting, the shells are caught up by overhead tongs which place them in jiggle-proof "tote boxes," like wooden egg boxes, and a conveyor carries them to the melt-loading building. The conveyors, which were specially designed for this type of plant, link together the various process buildings of the loading line. These buildings are located far apart for safety, and extend for more than a mile. They have two "tracks" of rollers over which the tote boxes are moved by "pusher" arms extending from a moving chain as a sort of "third rail." The conveyors are explosion-proof and are housed in corrugated asbestos siding and roofing. A conveyor also carries TNT, packed in wooden boxes, to the melt-loading building from another part of the plant. The TNT is melted on fireless stoves, heated by steam, in rooms on the second story, and the liquid is piped downstairs into ladles from which it is poured by hand into the shells. The shells are conveyed to another building where they are cooled and filling completed. Then they are taken to a drilling building where a bore through the solidified TNT is made in the nose of the shell for the booster and fuse. The motors which turn the drills are powdered by compressed air and have sparkless bearings. After being drilled, the shells are placed in storage magazines at the plant, ready for trans-shipment to various ordnance depots. The plant consists of more than 500 buildings located on a site covering 20,000 acres, and has 75 miles of railroad tracks and 75 miles of electric lines. Its power plant can furnish electricity sufficient to meet the needs of a city larger than Burlington, Iowa. The plant has its own water supply. The entire area is surrounded by 25 miles of wire fence seven feet in height, while inner areas are similarly fenced. The whole is illuminated at night by flood lights. Materials used for construction include 13,000,000 board feet of lumber, 3,600 tons of reinforcing steel, 181,000 railroad ties and 65,000 cu. yd. of cement. There are more than 100 miles of roads, 40 miles of water piping, seven miles of steam heat lines and 15 miles of sewage pipe lines. Experimentation and research work conducted by the Ordnance Department of the army at Picatinny Arsenal, Dover, N. J., for many years, as well as close collaboration between the army and its contractors, have gone into the design.

Short-Wave Radiophones Speed up Fire-Fighting.—A number of new radio devices are helping to increase the mobility and effectiveness of Forest Service fire fighting forces, the U. S. Department of Agriculture reports. Readily portable and of extremely light but tough construction, a variety of short-wave voice radiophones have been devised by the Department's Forest Service to meet the demands of fire-fighting forces on the National Forests. The radio equipment serves ground crews and smoke-chasers as well as the smoke-jumpers who parachute to back country fires from airplanes. Forest Service radios, however, find many other uses, the most recent call for them being received from the American Geographical Society for use on an expedition that will explore and map an area about 200 miles northwest of White Horse near the Canadian-Alaskan boundary this summer. The Short-wave outfits to be used by the expedition weigh twenty-one pounds, have a working range of twenty miles, and are the type used by the Forest Service for fire crews, rangers, guards and pack strings. Some of them will be dropped by parachutes with other supplies in localities that members of the mapping party may not reach until some weeks later, and are therefore expected to endure rough treatment by curious bears. A number of State and Federal forest protection agencies, British Columbia and Australia forestry agencies, and several non-forestry agencies use some Forest Service type radio equipment. Approximately 3,200 portable voice radiophones are now used in protecting the National Forests. The small set weighs less than six pounds, and is about three-quarters the size of a loaf of sandwich bread. This small transmitting and receiving outfit is carried by the smoke-jumpers so that they can talk to the delivery plane or call headquarters when they have parachuted to a fire. A bell-ringing radio for lookout towers devised about two years ago has been placed in more than two hundred locations, and radio "wave sprinklers" or automatic radio relay stations—of which several are already in use—are being installed as rapidly as possible. Operating automatically to re-broadcast messages from smaller radios, the relay station will be seen on a number of mountain tops this summer. Its antennæ of metal cross-arm and upright in the shape of a cross aids searching parties or fire-fighters unable to communicate with each other or with headquarters except by means of its power. The automatic stations require infrequent visits from attendants and make it possible for field crews to carry light instead of heavy radio equipment. A mobile radio transmitter costing only a few dollars and using a fish-pole type antennæ is employed on fire trucks and other vehicles. Trucks dispatched to a fire can be stopped if the alarm is found to be false, or re-routed to more serious outbreaks, or quick contact can be established with fire crews working on roads or in situations where they can be reached by telephone.

W. P.

Footprints 100,000,000 Years Old. (*The Scientific Monthly*, Vol. LIII, No. 3, Whole No. 312.)—Further evidence of the prehistoric monsters that roamed the earth millions of years ago, a group of dinosaur footprints perfectly preserved in limestone, has been uncovered in Bandera County, Texas, by a WPA paleontological project sponsored by the University of Texas. Considerable scientific interest has been aroused by the find, as these tracks are the first ones that so far have been discovered in a condition suitable for scientific study. Also interesting is the fact that both the five-toed prints of the huge sauropod or herbivorous dinosaur and the three-toed tracks of the smaller but ferocious carnivorous type were found in the same location. The tracks were found deeply imbedded in a Cretaceous limestone layer underlying some twelve feet of soil along the bank of the West Verde Creek, a few miles southwest of Bandera, Texas. WPA workers, under the supervision of Roland T. Bird of the American Museum of Natural History, carefully cut back the top layers of the soil and gravel and laid bare the prints. The tracks are now being studied and preserved and specimens will be displayed at the American Museum of Natural History in New York City and at the University of Texas

Memorial Museum at Austin. To the trained eye of the scientist the giant five-toed tracks, along the West Verde Creek, tell a story of a whole herd of sauropod dinosaurs which millions of years ago sloughed through the soft, warm mud of an inland sea covering much of Texas. The tracks give evidence of possibly eight or nine of these huge 50-foot-long quadrupeds which belong to the same group as the well-known Brontosaurus. The imprints of one baby belonging to this group were also found. A perfect row of three-toed, carnivorous dinosaur tracks, cut some three inches deep in the limestone layer, were found. These prints, looking like huge three-toed bird tracks, proceed for fifteen five-foot strides along the exposed portion. Among the carnivore tracks there are also those of a baby, probably no larger than a kangaroo, according to estimates. These prints give every evidence of being those of the erect predatory dinosaurs which roamed in packs and preyed upon the slower herbivorous sauropods. It is the curiously rounded, five-toed prints of the mammoth sauropod which has caused the most scientific interest, however. Measurements made at the West Verde site indicate that the largest footprint was 32 inches from heel to toe and that this mammoth amphibian walked with a nine-foot stride. From these measurements it is estimated that the largest of this group was approximately 14 feet high at the hips, was about 50 feet long and weighed more than 10 tons. Although many fossil remains of the giant sauropod, of which Brontosaurus, the "thunder-lizard," is perhaps the best representative, have been discovered in the western and southwestern portion of the United States and Canada, no clear-cut footprints, adaptable to scientific study, have been uncovered before. This is probably due to the fact that the amphibious sauropod spent most of his time in the water, feeding upon marine vegetation; and the mud flats over which he occasionally wandered were subject to wave action and other elements which would destroy the tracks.

W. P.

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Drycolene. (*General Electric Review*, Vol. 44, No. 7.)—Drycolene, the new atmosphere gas for heat-treating metals announced at the National Metal Exposition last fall, is now being used successfully by several industrial plants for heat-treating their steel products without surface decarburization. The new Drycolene gas is the latest advancement in protective atmospheres for such operations as the scale-free hardening, bright annealing, sintering, and electric-furnace brazing of high-carbon steels in which surface decarburization cannot be permitted. In the laboratory, the ideal gas for this purpose is dry nitrogen, but dry nitrogen is impractical for large-sized furnaces since their atmosphere cannot be kept sufficiently free of carbon dioxide, water vapor, or infiltered air. The presence of carbon monoxide in Drycolene, however, opposes the decarburizing action of these impurities. Steel hardened in Drycolene has been found to be hard right to the surface and has passed such tests for traces of surface decarburization as the Rockwell N ("Superficial") test, weight-change measurements, and photomicrographs. For example, all three tests were made on SAE-52100 and SAE-1090 steels. Samples were heated in Drycolene for two hours at 1500 F., and quenched. Weight-change measurements showed slight increases in weight, indicating no decarburization. Rockwell hardness-comparison tests gave slightly higher converted "superficial" (N) values than the "C" readings, indicating no decarburization. And photomicrographs showed absolute uniformity of structure extending right to the surfaces, which is usually further proof of no decarburization.

W. P.

Radio Short Waves Advance Behind Secrecy Curtain of War.—Behind the curtain of mystery which war drops on scientific research to guard devices developed for military purposes, radio engineers report it is no secret that outstanding advances are being made in short wave broadcasting. Spurred by the vital necessity of international communications, American research and ingenuity are accomplishing new wonders in radio. By means of electrically steerable aerials fed by high power, the National Broadcasting Company is putting Uncle Sam in a dominant position on the international radio map, hurling spoken words across the hemispheres with efficiency undreamed of during World War I. Since the European War broke out, America's horizon of steel towers and tall wooden masts has widened in the interests of national defense and international communications. Mindful of the importance of short wave service, the National Broadcasting Company has redoubled its efforts around the clock, operating a minimum of 16 hours a day, and at times 24 hours. The N. B. C. transmitters, WRCA—WNBI at Bound Brook, N. J., now are "pumping" 50,000 watts from early morning until late into the night to accommodate the time zones of the different nations, and thereby gain the advantages of the most favorable listening periods, especially in Europe and Latin America. At Bound Brook nearly 70 acres are devoted exclusively to international transmitting aerials. The site is rectangular in shape with the long dimension facing in the general direction of the Latin American countries. Raymond F. Guy, Radio Facilities Engineer of the N. B. C., in discussing the latest developments of international broadcasting in the *R. C. A. Review* explains that directive aerials are designed with the proper compromise between power gain and beam width, because one is obtained at the expense of the other. For instance, a beam broad enough to "searchlight" over all of South America would have such a low power gain that it would not provide the strong signal intensity required for satisfactory service. Mr. Guy points out that the design of aerials of very high power gain presents no special problem itself. In fact, he says, it would be a comparatively simple matter to increase the power gain to the point where a somewhat higher concentration of field intensity is obtained in one area at the excessive sacrifice of adjoining areas of importance.

R. H. O.

Powerful Ultraviolet Light Sources.—J. H. LAUB (*Electrical Engineering*, Vol. 60, No. 8).—The advent of the high-pressure vapor lamp with self-lighting actuated electrodes has made possible the development of new types of ultraviolet generators of high power and large size, which have become a very important tool for a number of industrial applications. First introduced in ultraviolet lamps for therapeutic and prophylactic use, the high-pressure quartz mercury-vapor lamp has been developed considerably further in size and power and is finding new and interesting uses in commercial irradiation processes. The new lamp with activated electrodes is very simple in its design. It consists of a tubular envelope transmittant to ultraviolet, preferably of clear fused quartz and two activated electrodes which are sealed to the ends of the tube. The electrodes usually are made of coiled tungsten wire and are coated with an activation material that facilitates the emission of electrons at elevated temperatures. Free barium and barium oxide, among others, are activation agents commonly used in tubes of this type. Instead of tungsten, cup-shaped and coated nickel electrodes are employed in certain types. A form of vacuum seal that has proved very satisfactory for these lamps consists of a thin molybdenum foil, approximately 1/1000 inch thick and several millimeters wide, which is fused vacuum tight into the quartz and which is capable of carrying an electrical current of several amperes to the electrodes. Graded seals have also been used employing several steps of glasses between the quartz envelope and the sealing glass around a tungsten lead-in wire. In manufacturing, the tube is carefully degassed and filled with a few droplets of mercury and a starting gas, usually argon of several millimeters pressure. When electric power is supplied the starting gas breaks down and for several seconds the initial discharge is carried by the starting gas. A high starting current warms up the electrodes and the heat and intense ion bombardment gradually vaporize the mercury so that a steadily increasing share of the discharge is taken over by the mercury vapor. With increasing temperature the pressure of the mercury vapor rises and after several minutes all the mercury is evaporated. Pressure, wattage and intensity remain constant, after equilibrium is reached, as long as the cooling conditions are not altered.

R. H. O.

Poison Smudge Patented.—Preliminary tests in the U. S. Department of Agriculture laboratories show that two insecticidal materials, rotenone and pyrethrum, heretofore used only as sprays or dusts, can be converted easily into fumigants that may be even more deadly. Tests of these fumigants in apartment houses, stores, hotels, and private houses are under way. Fumigation has long been important as a method of controlling insects. Many of the best fumigating materials, such as hydrocyanic acid and carbon disulphide, are poisonous to man as well as to insects, and call for great care in handling them. Pyrethrum and rotenone—highly toxic to insects but not to man—volatilize only at high temperatures, which so far has prevented their use as fumigants. The Bureau of Entomology and Plant Quarantine now finds that spraying a solution of rotenone or pyrethrum on to a hot plate may be the answer to the problem of converting either into an effective fumigant. The solution, hitting the hot surface, rises instantaneously as a thick smoke or fog—a so-called "aerosol"—that remains suspended in the air for several hours. In the laboratory rotenone and pyrethrum aerosols were very poisonous to flies and mosquitoes. How effective they will be against these and other common household insect pests in rooms where furniture, carpets, and cracks offer the insects some protection remains to be proved—also the effects of the aerosols on wall paper, fabrics and furniture. W. N. SULLIVAN and L. D. GOODHUE, who developed the method have applied for a public service patent.

R. H. O.

Modern Developments in Medicine and Surgery.—The wide variety of Steinmetz's interests in scientific, technical, and cultural developments gives appropriateness to the diversity of subjects presented in the Steinmetz Memorial Lectures. *General Electric Review*, Vol. 44, No. 7 contains a portion of the Fourteenth Steinmetz Memorial Lecture delivered by FRANK HOWARD LAHEY, M.D., Sc.D., of the Department of Surgery, The Lahey Clinic, Boston, Mass. The subject is interesting to everyone, whatever his profession; and to the engineer and physicist it will give an added satisfaction in affording an opportunity to see how long-familiar laws and principles function. Dr. Lahey discusses the effects of chemicals on bacteria, the vitamins, glands, the use of helium in medicine, plastic surgery, nerve grafts, etc. Of interest to those interested in electricity, Dr. Lahey cites a method of making a new hip joint which brings about an outgrowth of bone, both in the socket and in the head of the joint. These two outgrowths of bone sometimes fuse and bring about fixation, resulting in a permanently stiff hip. It is possible by means of a surgical operation to expose this hip joint, to chisel the head of the bone out, to scrape away the socket until its surface is perfectly smooth, and then by means of files and rasps to so smooth the head that it is perfectly smooth and will fit into the socket of the joint and move freely. It is useless, however, to put this head back in the socket because further outgrowths of bone will promptly result in recurring fixation. All operations upon bones have been greatly benefited by the discovery on the part of Dr. Charles Venable of San Antonio, that the reason metals are not well tolerated by the human tissues is related to the fact that most metals produce electrolysis in tissues. Dr. Venable, by the combination of metals, developed a nonelectrolytic metal called vitallium. This material, owing to the fact that it is nonelectrolytic, is now well tolerated by the tissues and so, after the socket of the hip joint has been smoothed out and after the head has been rasped off until it is smooth, a vitallium metal cup can be placed over the head of the hip bone, the head then reduced into the hip joint, the wound closed and a permanent metal movable joint made.

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R. H. O.

New Industrial Uses for Cotton. (The National Farm Chemurgic Council, *News Bulletin*, August 25, 1941.)—Two new applications of America's great cotton crop, whose export markets have largely been cut off by the war, are announced by the Department of Agriculture as an outcome of its research program. One is an extension of smokeless powder manufacture; the other is a wax obtained from an unusual variety of green cotton. The manufacture of smokeless powder had depended hitherto on supplies of cotton linters, the short fuzzy fibers that are removed from the cotton seed after the ginning process has taken off the staple. These short fibers were best for the nitrating process that converted the cellulose of cotton into explosive cellulose nitrate. When attempts were made to use long fibers of cotton staple in the same process, it was found that the fibers tended to become entangled and thus quite literally to "tie up" production. The Bureau of Agricultural Chemistry and Engineering, at its Southern Regional Research Laboratory, proceeded to develop machines like giant lawnmowers which would cut up the staple cotton into the short shreds best suited for nitration. One such machine, the department reports, can handle two tons of cotton per hour. By use of this machinery the great supplies of smokeless powder now needed by the Army and Navy for big guns, antiaircraft artillery and rifles can be obtained from regular cotton. Linters would still be used for such purposes as rayon, cellulose acetate plastics and nitro-cellulose lacquers. The second development of interest to cotton growers is the possibility of growing an unusual variety of cotton for its wax rather than its cellulose. This variety, known as Arkansas Green Lint, is reported to yield as much as 17 per cent. of wax instead of the usual one-half of 1 per cent. In collaboration with a chemical company, which is growing five acres of the green-lint cotton in South Carolina, scientists of the Agriculture Department are trying to produce a hard wax suitable for polishing shoes, furniture, automobiles and floors.

W. P.

N. Y. U. College of Engineering Adds New Apparatus.—A high voltage surge generator, one of the largest in an eastern university and the only on in the metropolitan area, has been constructed at the New York University College of Engineering by a graduate student under the supervision of Professor Harold Torgersen of the electrical engineering department, it was announced by Dean Thorndike Saville. Capable of generating 350,000 volts, the generator was a project of Ralph Armington of Medford, Massachusetts, who is working toward a master's degree in electrical engineering. It becomes the second unit in the newly established high voltage laboratory at the college. The first, installed last fall when the laboratory was opened, is a high voltage transformer. The apparatus will be used in high voltage research for the testing of insulating materials and insulators, Dean Saville said. It consists of 15 condensers, charged in parallel in groups of three, and discharged in series through five small intermediate sphere gaps. The voltage is measured by a 12 inch sphere gap. The appratus occupies an area approximately thrity-six square feet and in addition to the condensers, the "giant" measuring gap has control switches and a device by which the gap can be widened and closed from a safe distance by the operator of the machine. While the apparatus has been designed and constructed chiefly for the use of graduate students and research engineers, it also has certain applications in undergraduate electrical engineering study especially in the study of transient voltages. Graduate research in which the machine will be utilized will concern the effect of surge voltages on electrical equipment and the study of the generation of surge voltages. In conjunction with Professor Philip Greenstein, also of the department of electrical engineering, Professor Torgersen has developed a high speed, high voltage cathode ray oscillograph which will be used with the surge generator.

R. H. O.

Mining in Alaska in 1940.—Mines in Alaska produced minerals worth $28,470,000 in 1940, as against $25,296,000 in 1939, according to an announcement made by the Geological Survey, United States Department of Interior. Some of the significant facts concerning the Alaskan Mineral industry in 1940 are summarized as follows. The total value of minerals produced from Alaskan mines in 1940 was greater than in any other year except the four years of the first World War, 1915 to 1918. The total mineral output of Alaska in 1940 exceeded that of 1939 by about 12½ per cent. and the increase is not regarded as being due to unusually favorable conditions that may not soon be repeated but appears to mark a level that can be maintained or bettered under such normal conditions as may reasonably be expected. The value of the gold produced from the mines of the Territory in 1940 marked an all-time high, surpassing even the so-called "boom days" of the great gold rush to Alaska. The quantity of coal mined exceeded that of any preceding year and the value of silver produced appears to have been more than that produced in 1939, although the quantity was less. Slight decreases were apparent in the quantity and value of the copper, lead and lime rock produced in 1940 as compared with the record for 1939, but the total value of these commodities constitutes only a little more than one-half of one per cent. of the total mineral output of the territory.

R. H. O.

Upping Efficiency With Air Conditioning. (*Heating, Piping and Air Conditioning*, Vol. 13, No. 9.)—Blemishes in newspicture negatives due to variations in developing solution temperatures have been practically eliminated in the modern photo laboratories of Philadelphia's *Evening Bulletin*, since air conditioning was installed. In addition, elapsed time from exposed negative to final print has been cut down to 7½ min. with the help of air conditioning and other modern devices. The problem of quick photographic processing is an acute one in these days of fast picture work and high speed news publishing. Rapid developing, fixing and washing of prints has been achieved in the completely air-conditioned darkroom through the introduction of up-to-date methods. Even hot air and fumes generated by carbon arcs used in the printing room are removed through forced ventilation. Films are dried in a centrifugal dryer. Electrically heated ovens are used to dry points not marked "rush." Air-conditioning was first installed at the *Bulletin* in 1933, when the city room and editorial offices were modernized. In 1936, the paper's ground floor public space was air-conditioned. A year later, a modernization program involving the entire building was launched. Cooling equipment includes eight refrigeration units with a total cooling capacity of 350 tons. One of the unusual features of the installation was that the refrigeration machines had to be situated in a circular clock tower atop the 10 story *Bulletin* building. An unique "spider web" foundation of structural steel was built to provide suitable vibration and sound isolation.

R. H. O.

California Magnesium Plant Starts Production. (*Iron Age*, Vol. 148, No. 9.)—Production of magnesium from magnesite by the Hansgirg process was started experimentally recently in the first unit of the new plant of the Chemical Engineering Division, Todd California Shipbuilding Corp., Los Altos, Cal. This new operation is being watched with keen interest as a source of cheap magnesium. The basic idea of the Hansgirg process is to reduce magnesium oxide with carbon at a high temperature, dilute and cool the reaction products with a cold inert gas, and thus recover metallic magnesium. The reversible reaction $MgO + C \rightleftarrows Mg + CO$ is forced to the right by the high temperature, 3600° F., of a three-phase electric arc furnace. If the reaction produced is cooled normally, the reverse reaction occurs and the yield of metallic magnesium is negligible. Sudden chilling and dilution of the magnesium and carbon monoxide mixture, however, minimizes the reaction between the two and gives a high yield of metal. United States production of magnesium is rising rapidly under the stimulus of defense demands, and this new operation is being watched with utmost interest because of the importance of magnesium in national defense and of the basic cheapness of the process for recovering metal from magnesite directly. Output in U. S. in 1935 was 2120 tons, which rose to 5325 tons by 1939. During 1940, the estimated production was 6250 tons, while the 1939 estimated world production totaled 36,159 tons. Plans now under consideration provide for an ultimate U. S. production of about 50,000 tons annually.

R. H. O.